

IN THE MATTER OF an International
Patent Application
in the name of
BASF Aktiengesellschaft
filed under No. PCT/EP03/11144, and
IN THE MATTER OF an Application
for a U.S. Patent.

RWS Group Ltd, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England, hereby solemnly and sincerely declares that to the best of its knowledge and belief, the following document, prepared by one of its translators competent in the art and conversant with the English and German languages is a true and correct translation of the Patent Application filed under No. PCT/EP03/11144

by BASF Aktiengesellschaft

in Germany on November 20, 2002

for "Multimetal oxide materials"

and the Official Certificate attached thereto.

Date: December 12, 2005

A handwritten signature in black ink, appearing to be 'S. Anthony', with a stylized, cursive script.

S. ANTHONY

Director

For and on behalf of RWS Group Ltd

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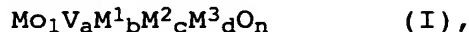
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Letang

We claim:-

1. A multimetal oxide material of the stoichiometry I

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where

- 10 M^1 is at least one of the elements from the group consisting of Te and Sb;
 M^2 is at least one of the elements from the group consisting of Nb, Ti, W, Ta and Ce;
 M^3 is at least one of the elements from the group
15 consisting of Pb, Ni, Co, Bi, Pd, Ag, Pt, Cu, Au, Ga, Zn, Sn, In, Re, Ir, Sm, Sc, Y, Pr, Nd and Tb;
 a is from 0.01 to 1,
 b is from > 0 to 1,
20 c is from > 0 to 1,
 d is from > 0 to 0.5 and
 n is a number which is determined by the valency and frequency of the elements other than oxygen in (I),
25 whose X-ray diffraction pattern has reflections h , i and k whose peaks are at the diffraction angles (2θ) $22.2 \pm 0.5^\circ$ (h), $27.3 \pm 0.5^\circ$ (i) and $28.2 \pm 0.5^\circ$ (k),
— the reflection h being the one with the strongest
30 intensity within the X-ray diffraction pattern and having a full width at half height (FWHH) of not more than 0.5° ,
— the intensity P_i of the reflection i and the intensity P_k of the reflection k satisfying the relationship $0.65 \leq R \leq 0.85$, where R is the intensity ratio defined by the
35 formula

$$R = P_i / (P_i + P_k)$$

and

- 40 — the FWHH of the reflection i and that of the reflection k being each $\leq 1^\circ$,

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wherein the at least one multimetal oxide material (I) is one whose X-ray diffraction pattern has no reflection with the peak position $2\theta = 50.0 \pm 0.3^\circ$.

- 5 2. A multimetal oxide material as claimed in claim 1, wherein $0.67 \leq R \leq 0.75$.
3. A multimetal oxide material as claimed in claim 1, wherein $0.69 \leq R \leq 0.75$.
- 10 4. A multimetal oxide material as claimed in claim 1, wherein $0.71 \leq R \leq 0.74$.
5. A multimetal oxide material as claimed in claim 1, wherein R
15 = 0.72.
6. A multimetal oxide material as claimed in any of claims 1 to 5, wherein its specific surface area is from 11 to 40 m²/g.
- 20 7. A multimetal oxide material as claimed in any of claims 1 to 6, wherein its X-ray diffraction pattern has further reflections with their peak position at the following fraction angles 2θ :
- 25 $9.0 \pm 0.4^\circ$ (l),
 $6.7 \pm 0.4^\circ$ (o) and
 $7.9 \pm 0.4^\circ$ (p).
8. A multimetal oxide material as claimed in claim 7, wherein
30 its X-ray diffraction pattern has further reflections with their peak positions at the following diffraction angles 2θ :
- $29.2 \pm 0.4^\circ$ (m) and
 $35.4 \pm 0.4^\circ$ (n).
- 35 9. A multimetal oxide material as claimed in claim 8, wherein the intensity of the reflections h, i, l, m, n, o, p and q have the following intensities on the same intensity scale:
- 40 h = 100,
i = 5 to 95,
l = 1 to 30,
m = 1 to 40,
o = 1 to 30,
45 p = 1 to 30 and
q = 5 to 60.

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10. A multimetal oxide material as claimed in any of claims 1 to 9, wherein $a = 0.05$ to 0.6 .
11. A multimetal oxide material as claimed in any of claims 1 to 10, wherein $b = 0.01$ to 1 .
12. A multimetal oxide material as claimed in any of claims 1 to 11, wherein $c = 0.01$ to 1 .
13. A multimetal oxide material as claimed in any of claims 1 to 12, wherein $d = 0.0005$ to 0.5 .
14. A multimetal oxide material as claimed in any of claims 1 to 13, wherein
- $a = 0.1$ to 0.6 ;
 $b = 0.1$ to 0.5 ;
 $c = 0.1$ to 0.5 and
 $d = 0.001$ to 0.5 .
15. A multimetal oxide material as claimed in any of claims 1 to 14, wherein at least 50 mol% of the total amount of M^2 is Nb.
16. A multimetal oxide material as claimed in any of claims 1 to 14, wherein at least 75 mol% of the total amount of M^2 is Nb.
17. A multimetal oxide material as claimed in any of claims 1 to 14, wherein M^2 is exclusively Nb.
18. A multimetal oxide material as claimed in any of claims 1 to 17, wherein M^3 is at least one element from the group consisting of Ni, Co, Bi, Pd, Ag, Au, Pb and Ga.
19. A multimetal oxide material as claimed in any of claims 1 to 17, wherein M^3 is at least one element from the group consisting of Ni, Co, Pd and Bi.
20. A multimetal oxide material as claimed in any of claims 1 to 17, wherein M^1 is Te, M^2 is Nb and M^3 is at least one element from the group consisting of Ni, Co and Pd.
21. A multimetal oxide material which contains at least one multimetal oxide material as claimed in any of claims 1 to 20 and whose X-ray diffraction pattern has no reflection with the peak position $2\theta = 50.0 \pm 0.3^\circ$.

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22. A multimetal oxide material as claimed in claim 21, in which the multimetal oxide material (I) is present in a form diluted with at least one finely divided material from the group consisting of silica, titanium dioxide, alumina, zirconium oxide and niobium oxide.
23. A multimetal oxide material which contains $\geq 80\%$ by weight of at least one multimetal oxide material as claimed in any of claims 1 to 20 and whose X-ray diffraction pattern has a reflection with the peak position $2\theta = 50.0 \pm 0.3^\circ$.
24. A process for the heterogeneously catalyzed partial gas-phase oxidation of at least one saturated or unsaturated hydrocarbon, wherein the catalytically active material used is at least one multimetal oxide material as claimed in any of claims 1 to 23.
25. A process as claimed in claim 24, wherein the hydrocarbon is propane, propene or a mixture of propane and propene.
26. A process for the heterogeneously catalyzed partial gas-phase ammoxidation of at least one saturated or unsaturated hydrocarbon, wherein the catalytically active material used is at least one multimetal oxide material as claimed in any of claims 1 to 23.
27. A process as claimed in claim 26, wherein the hydrocarbon is propane, propene or a mixture of propane and propene.
28. The use of at least one multimetal oxide material as claimed in any of claims 1 to 23 as a catalyst for a heterogeneously catalyzed partial oxidation and/or ammoxidation of at least one saturated and/or unsaturated hydrocarbon.
29. A process for the preparation of a multimetal oxide material as claimed in any of claims 1 to 20, wherein an intimate dry blend is produced from sources of its elemental constituents, said dry blend is calcined at from 350 to 700°C and the resulting product is washed with an aqueous solution of an organic and/or inorganic acid.

Multimetal oxide materials

The present invention relates to multimetal oxide materials of
5 the stoichiometry I



where

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M^1 is at least one of the elements from the group consisting of Te and Sb;

M^2 is at least one of the elements from the group consisting of Nb, Ti, W, Ta and Ce;

15 M^3 is at least one of the elements from the group consisting of Pb, Ni, Co, Bi, Pd, Ag, Pt, Cu, Au, Ga, Zn, Sn, In, Re, Ir, Sm, Sc, Y, Pr, Nd and Tb;

a is from 0.01 to 1,

20 b is from > 0 to 1,

c is from > 0 to 1,

d is from > 0 to 0.5 and

n is a number which is determined by the valency and frequency of the elements other than oxygen in (I),

25

whose X-ray diffraction pattern has reflections h, i and k whose peaks are at the diffraction angles (2θ) $22.2 \pm 0.5^\circ$ (h), $27.3 \pm 0.5^\circ$ (i) and $28.2 \pm 0.5^\circ$ (k),

30 - the reflection h being the one with the strongest intensity with in the X-ray diffraction pattern and having a full width at half height (FWHH) of not more than 0.5° ,

- the intensity P_i of the reflection i and the intensity P_k of the reflection k satisfying the relationship $0.65 \leq R \leq 0.85$,

35 where R is the intensity ratio defined by the formula

$$R = P_i / (P_i + P_k)$$

and

40 - the FWHH of the reflection i and that of the reflection k being each $\leq 1^\circ$, and wherein

the at least one multimetal oxide material (I) is one whose X-ray diffraction pattern has no reflection with the peak position $2\theta =$

45 $50.0 \pm 0.3^\circ$.

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The present invention furthermore relates to the preparation of multimetal oxide materials (I) and their use for the heterogeneously catalyzed partial oxidation and/or ammoxidation of saturated and/or unsaturated hydrocarbons.

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Multimetal oxide materials of the stoichiometry (I) and having a stoichiometric coefficient $d = 0$, which are obtainable by calcining an intimate dry blend of their elemental constituents in an oxygen-containing atmosphere, are disclosed, for example, 10 in EP-A 318295. They are suitable, for example, for the heterogeneously catalyzed ammoxidation of propane or isobutane for the preparation of acrylonitrile and methacrylonitrile, respectively, and typically have a high amorphous fraction in their structure.

15

EP-A 512846 discloses that the performance of multimetal oxide materials of EP-A 318295 can be improved with respect to their use as catalysts for the partial ammoxidation of saturated hydrocarbons by adding promoter elements M^3 .

20

EP-A 529853, EP-A 603836, EP-A 608838, EP-A 767164, EP-A 895809 and EP-A 962253 disclose multimetal oxide materials of the stoichiometry (I) and having a stoichiometric coefficient $d = 0$ which are obtainable by calcining an intimate dry blend of their 25 elemental constituents in an atmosphere substantially free of oxygen. In comparison with the multimetal oxide materials of EP-A 318295 and of EP-A 512846, they are even more suitable as catalysts for the heterogeneously catalyzed partial ammoxidation and/or oxidation of saturated hydrocarbons. The latter in 30 particular when the intimate dry blend was produced as a catalyst precursor by spray drying.

In the publications cited, this is attributed to the fact that, as a result of their preparation, these multimetal oxide 35 materials are present in crystalline form substantially with a specific crystal structure whose X-ray diffraction pattern has reflections of strong intensity at the 2θ peak positions $22.1 \pm 0.3^\circ$, $28.2 \pm 0.3^\circ$, $36.2 \pm 0.3^\circ$, $45.2 \pm 0.3^\circ$ and $50.0 \pm 0.3^\circ$.

40 DE-A 19835247, EP-A 1090684 and WO 0206199 disclose that the abovementioned specific crystal structure forms only one crystalline phase in which such multimetal oxide materials can occur. In the abovementioned literature, this crystalline phase is referred to as a rule as the k-phase.

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A second specific crystal structure in which the relevant multimetal oxide materials can occur is referred to as a rule as the i-phase. According to the abovementioned publications, its X-ray diffraction pattern has inter alia reflections of strong
5 intensity at the 2θ peak positions $22.2 \pm 0.4^\circ$, $27.3 \pm 0.4^\circ$ and $28.2 \pm 0.4^\circ$ but, in contrast to the k-phase, no reflection at the 2θ peak position $50.0 \pm 0.3^\circ$.

For example, according to EP-A 529853, EP-A 608838 and
10 EP-A 603836, the k-phase is responsible for the catalytic activity of the multimetal oxide materials mentioned there.

In the method of preparation described above, usually neither pure k-phase nor pure i-phase is obtained, but mixed crystal
15 structures which are an intergrown mixture of k- and i-phase.

In EP-A 1192987, EP-A 1192986, EP-A 1192983 and EP-A 1192982, such mixed crystal multimetal oxide materials are prepared and it is shown that their performance can be improved with respect to
20 their use as catalysts for the partial ammoxidation and/or oxidation of saturated hydrocarbons by adding promoter elements M^3 , the decisive role being attributed to the k-phase.

In contrast, JP-A 11-169716 ascribes a decisive role for the
25 catalytic activity of such mixed crystal multimetal oxide materials in the partial ammoxidation of saturated hydrocarbons to both the k-phase and the i-phase. Accordingly, the k-phase is responsible for a satisfactory selectivity of the nitrile formation and the i-phase for sufficient conversion of the
30 saturated hydrocarbon.

In "Ammoxidation of propane over Mo-V-Nb-Te mixed oxide catalysts" from "Spillover and Migration of Surface on Catalysts", ed. by Can Li and Quin Xin, Elsevier Science B.V.
35 (1997), page 473 et seq., the inventors of JP-A 11-169716 reinforce this concept, which is also supported by DE-A 19835247 and EP-A 895089.

In contrast, JP-A 7-232071 and WO 0206199 disclose that
40 multimetal oxide material present exclusively in the i-phase structure are also suitable as catalysts for the heterogeneously catalyzed partial ammoxidation and/or oxidation of saturated hydrocarbons.

45 Furthermore, experiments have been carried out in which it is shown that multimetal oxide materials present exclusively in the k-phase structure are catalytically inactive and support the

concept of JP-A 11-169716, according to which the i-phase is responsible for the activity and the k-phase only for maximizing the selectivity.

- 5 WO 00/29106, WO 00/29105, WO 00/38833 and WO 00/69802 disclose promoter-containing multimetal oxide materials which have a substantially amorphous structure which appears in the X-ray diffraction pattern in the form of very broad reflections, and which are likewise recommended as catalysts for partial
10 oxidations.

DE-A 10118814 and PCT/EP/02/04073 disclose that pure i-phase multimetal oxide materials are also suitable catalysts for partial oxidations of unsaturated hydrocarbons.

- 15 JP-A 8-57319 discloses that Mo and/or V-containing multimetal oxide materials can be activated by treatment with acid.

- The disadvantage of the given prior art, however, is that it
20 firstly does not answer the question as to whether the promoters incorporated both into the i-phase and into the k-phase and whether they influence the catalytic activity of the two phases and secondly their multimetal oxide materials are not completely satisfactory, with regard to the selectivity of the formation of
25 the desired product, as catalysts for the heterogeneously catalyzed partial oxidation and/or ammoxidation of saturated and/or unsaturated hydrocarbons.

- It is an object of the present invention to answer the unanswered
30 question and to provide multimetal oxide materials improved in the context of the object.

- We have found that this object is achieved by the multimetal oxide materials (I) defined at the outset (all data based on an
35 X-ray diffraction pattern in this document relate to an X-ray diffraction pattern produced using CuK_α radiation as X-rays (Siemens diffractometer Theta-Theta D-5000, tube voltage: 40 kV, tube current: 40 mA, aperture V20 (variable), collimator V20 (variable), secondary monochromator aperture (0.1 mm), detector
40 aperture (0.6 mm), measuring interval $(2\theta): 0.02^\circ$, measuring time per step: 2.4 s, detector: scintillation counter); in this document, the definition of the intensity of a reflection in the X-ray diffraction pattern is based on the definition stated in DE-A 19835247, DE-A 10122027 and in DE-A 10051419 and
45 DE-A 10046672; the same applies to the definition of the full width at half height).

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According to the invention, preferably $0.67 \leq R \leq 0.75$ and very particularly preferably $R = 0.69$ to 0.75 or $R = 0.71$ to 0.74 or $R = 0.72$.

- 5 In addition to the reflections h, i and k, the X-ray diffraction pattern of novel multimetal oxide materials (I) generally also contains further reflections whose peaks are at the following diffraction angles (2θ):

- 10 $9.0 \pm 0.4^\circ$ (l),
 $6.7 \pm 0.4^\circ$ (o) and
 $7.9 \pm 0.4^\circ$ (p).

- It is furthermore advantageous if the X-ray diffraction pattern
15 additionally contains a reflection whose peak is at the diffraction angle (2θ) = $45.2 \pm 0.4^\circ$ (q).

- Frequently, the X-ray diffraction pattern of multimetal oxide materials (I) also contains the reflections $29.2 \pm 0.4^\circ$ (m) and
20 $35.4 \pm 0.4^\circ$ (n) (peak positions).

- If the reflection h is assigned to the intensity 100, it is advantageous, according to the invention, if the reflections i, l, m, n, o, p and q have the following intensities on the same
25 intensity scale:

- i: from 5 to 95, frequently from 5 to 80, in some cases from 10 to 60;
l: from 1 to 30;
30 m: from 1 to 40;
o: from 1 to 30;
p: from 1 to 30 and
q: from 5 to 60.

- 35 If the X-ray diffraction pattern of the novel multimetal oxide materials (I) contains any of the abovementioned additional reflections, the FWHH thereof is as a rule $\leq 1^\circ$.

- The specific surface area of the novel multimetal oxide materials
40 (I) is frequently from 1 to 40, often from 11 or 12 to 40, frequently from 15 or 20 to 40 or 30, m^2/g (determined by the BET method, nitrogen).

- According to the invention, the stoichiometric coefficient a of
45 the novel multimetal oxide materials (I) is preferably from 0.05 to 0.6, particularly preferably from 0.1 to 0.6 or 0.5, independently of the preferred ranges for the other

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stoichiometric coefficients of the multimetal oxide materials (I).

Independently of the preferred ranges for the other
5 stoichiometric coefficients of the multimetal oxide materials (I), the stoichiometric coefficient b is preferably from 0.01 to 1, particularly preferably from 0.01 or 0.1 to 0.5 or 0.4.

The stoichiometric coefficient c of the novel multimetal oxide
10 materials (I) is from 0.01 to 1, particularly preferably from 0.01 or 0.1 to 0.5 or 0.4, independently of the preferred ranges for the other stoichiometric coefficients of the multimetal oxide materials (I). A very particularly preferred range for the
15 stoichiometric coefficient c, which, independently of the preferred ranges for the other stoichiometric coefficients of the novel multimetal oxide materials (I), can be combined with all other preferred ranges in this document, is from 0.05 to 0.2.

According to the invention, the stoichiometric coefficient d of
20 the novel multimetal oxide materials (I) is preferably from 0.00005 or 0.0005 to 0.5, particularly preferably from 0.001 to 0.5, frequently from 0.002 to 0.3, often from 0.005 or 0.01 to 0.1, independently of the preferred ranges for the other stoichiometric coefficients of the multimetal oxide materials
25 (I).

Particularly preferred novel multimetal oxide materials (I) are those whose stoichiometric coefficients a, b, c and d are simultaneously in the following ranges:

30

a = from 0.05 to 0.6;
b = from 0.01 to 1 (or from 0.01 to 0.5);
c = from 0.01 to 1 (or from 0.01 to 0.5); and
d = from 0.0005 to 0.5 (or from 0.001 to 0.3).

35

Very particularly advantageous novel multimetal oxide materials (I) are those whose stoichiometric coefficients a, b, c and d are simultaneously in the following ranges:

40

a = from 0.1 to 0.6;
b = from 0.1 to 0.5;
c = from 0.1 to 0.5; and
d = from 0.001 to 0.5 or from 0.002 to 0.3 or from 0.005 to 0.1.

45

M¹ is preferably Te.

All of the abovementioned applies in particular when at least 50 mol% of the total amount of M^2 is Nb, very particularly preferably when at least 75 mol% or 100 mol% of the total amount of M^2 is Nb.

- 5 However, independently of the meaning of M^2 , it also applies in particular when M^3 is at least one element from the group consisting of Ni, Co, Bi, Pd, Ag, Au, Pb and Ga or at least one element from the group consisting of Ni, Co, Pd und Bi.
- 10 However, all of the abovementioned also applies in particular when at least 50 mol% of the total amount of M^2 or at least 75 mol% or 100 mol% is Nb and M^3 is at least one element from the group consisting of Ni, Co, Bi, Pd, Ag, Au, Pb and Ga.
- 15 However, all of the abovementioned also applies in particular when at least 50 mol% or at least 75 mol% or 100 mol% of the total amount of M^2 is Nb and M^3 is at least one element from the group consisting of Ni, Co, Pd and Bi.
- 20 Very particularly preferably, all statements regarding the stoichiometric coefficients apply when M^1 is Te, M^2 is Nb and M^3 is at least one element from the group consisting of Ni, Co and Pd.
- 25 Further stoichiometries suitable according to the invention are those which are disclosed for the multimetal oxide materials of the stoichiometry (I) in the prior art cited at the outset.

- The principle of a targeted process for the preparation of novel
- 30 multimetal oxide materials (I) is disclosed, for example, in WO 0206199 and the references cited in this publication. According to these, a multimetal oxide material which has the stoichiometry (I) but is a generally intimately integral mixed crystal system comprising an i-phase and other phases (e.g.
- 35 k-phase) is first produced in a manner known per se. The i-phase fraction can then be isolated from this mixture by washing out the other phases, e.g. the k-phase, with suitable liquids. Suitable such liquids are, for example, aqueous solutions of organic acids (e.g. oxalic acid, formic acid, acetic acid, citric
- 40 acid and tartaric acid), inorganic acids (e.g. nitric acid), and alcohols and aqueous hydrogen peroxide solutions. Furthermore, JP-A 7-232071 also discloses a process for the preparation of i-phase multimetal oxide materials.
- 45 Mixed crystal systems comprising i- and k-phases are obtained, as a rule, by the preparation processes described in the prior art (cf. for example DE-A 19835247, EP-A 529853, EP-A 603836,

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EP-A 608838, EP-A 895809, DE-A 19835247, EP-A 962253,
EP-A 1080784, EP-A 1090684, EP-A 1123738, EP-A 1192987,
EP-A 1192986, EP-A 1192982, EP-A 1192983 and EP-A 1192988).

According to these processes, a very intimate, preferably finely
5 divided, dry blend is produced from suitable sources of the
elemental constituents of the multimetal oxide materials and said
dry blend is thermally treated at from 350 to 700°C or from 400 to
650°C or from 400 to 600°C. The thermal treatment can in principle
be effected under an oxidizing, reducing or inert atmosphere. A
10 suitable oxidizing atmosphere is, for example, air, air enriched
with molecular oxygen or air depleted in oxygen. The thermal
treatment is, however, preferably carried out under an inert
atmosphere, i.e. for example under molecular nitrogen and/or
noble gas. Usually, the thermal treatment is effected at
15 atmospheric pressure (1 atm). Of course, the thermal treatment
can also be effected under reduced or superatmospheric pressure.

If the thermal treatment is effected under a gaseous atmosphere,
this may be either stationary or flowing. It preferably flows. In
20 general, the thermal treatment may take up to 24 hours or longer.

The thermal treatment is preferably first effected under an
oxidizing (oxygen-containing) atmosphere (e.g. under air) at from
150 to 400°C or from 250 to 350°C (= preliminary decomposition
25 step). The thermal treatment is then expediently continued under
inert gas at from 350 to 700°C or from 400 to 650°C or from 450 to
600°C. Of course, the thermal treatment can also be effected by
first pelleting the catalyst precursor material before its
thermal treatment (if necessary, after pulverizing and with or
30 without the addition of from 0.5 to 2% by weight of finely
divided graphite), then subjecting it to thermal treatment and
thereafter converting it into chips again.

The thorough mixing of the starting compounds can be effected in
35 dry or in wet form.

If it is effected in dry form, the starting compounds are
expediently used in the form of finely divided powders and, after
mixing and, if required, compaction, are subjected to the
40 calcination (thermal treatment).

However, the thorough mixing is preferably effected in wet form.
Usually, the starting compounds are mixed with one another in the
form of an aqueous solution (if required, in the presence of a
45 complexing agent; cf. for example DE-A 10145958) and/or
suspension. The aqueous material is then dried and is calcined
after the drying. The aqueous material is expediently an aqueous

solution or an aqueous suspension. The drying process is preferably effected immediately after the preparation of the aqueous mixture (particularly in the case of an aqueous solution, cf. for example JP-A 7-315842) and by spray drying (the exit
5 temperatures are as a rule from 100 to 150°C; the spray drying can be carried out by the cocurrent or countercurrent method), which results in a particularly intimate dry blend, especially when the aqueous material to be spray dried is an aqueous solution or suspension. However, it can also be dried by evaporating down
10 under reduced pressure, by freeze drying or by conventional evaporating down.

Suitable sources for the elemental constituents when carrying out the preparation of i-/k-phase mixed crystal multimetal oxide
15 materials by the method described above are all those which are capable of forming oxides and/or hydroxides on heating (if required in air). Of course, oxides and/or hydroxides of the elemental constituents may themselves be concomitantly used or exclusively used as such starting compounds, i.e. in particular
20 all starting compounds mentioned in the publications of the prior art considered are suitable.

Sources for the element Mo which are suitable according to the invention are, for example, molybdenum oxides, such as molybdenum
25 trioxide, molybdates, such as ammonium heptamolybdate tetrahydrate, and molybdenum halides, such as molybdenum chloride.

Suitable starting compounds to be concomitantly used according to
30 the invention for the element V are, for example, vanadium oxysulfate hydrate, vanadyl acetylacetonate, vanadates, such as ammonium metavanadate, vanadium oxides, such as vanadium pentoxide (V_2O_5), vanadium halides, such as vanadium tetrachloride (VCl_4) and vanadium oxyhalides, such as $VOCl_3$. Other vanadium
35 starting compounds which may be present are those which contain vanadium in the oxidation stage +4.

Sources of the element tellurium which are suitable according to the invention are tellurium oxides, such as tellurium dioxide,
40 metallic tellurium, tellurium halides, such as $TeCl_2$, and also telluric acids, such as orthotelluric acid H_6TeO_6 .

Advantageous antimony starting compounds are antimony halides, such as $SbCl_3$, antimony oxides, such as antimony trioxide (Sb_2O_3),
45 antimoninic acids, such as $HSb(OH)_6$, and also antimony oxide salts, such as antimony oxide sulfate $(SbO)_2SO_4$.

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Niobium sources suitable according to the invention are, for example, niobium oxides, such as niobium pentoxide (Nb_2O_5), niobium oxyhalides, such as NbOCl_3 , niobium halides, such as NbCl_5 , and also complex compounds of niobium and organic
5 carboxylic acids and/or dicarboxylic acids, e.g. oxalates and alcoholates. Of course, the niobium-containing solutions used in EP-A 895809 are also suitable as a niobium source.

Regarding all other possible elements (in particular Pb, Ni, Cu,
10 Co, Bi and Pd), suitable starting compounds are in particular their halides, nitrates, formates, oxalates, acetates, carbonates and/or hydroxides. Suitable starting compounds are often also their oxo compounds, e.g. tungstates, or the acids derived from these. Ammonium salts are also frequently used as starting
15 compounds.

Other suitable starting compounds are polyanions of the Anderson type, as described, for example, in Polyhedron Vol. 6, No. 2, pages 213-218, 1987. A further suitable literature source for
20 polyanions of the Anderson type is Kinetics and Catalysis, Vol. 40, No. 3, 1999, pages 401 to 404.

Other polyanions suitable as starting compounds are, for example, those of the Dawson and Keggin type. Preferably used starting
25 compounds are those which are converted into their oxides at elevated temperatures, either in the presence or in the absence of oxygen, possibly with liberation of gaseous compounds.

The i-/k-phase mixed crystal multimetal oxide materials
30 obtainable as described (pure i-phase multimetal oxides are obtained only by chance by the procedure described) can then be converted into novel multimetal oxides (I) by suitable washing in the manner described.

35 A high proportion of i-phase (and in advantageous cases substantially pure i-phase) is established in the preparation of precursor multimetal oxides (which can be converted into novel multimetal oxides (I) by the washing described) when they are prepared by the hydrothermal route, as described, for example, in
40 DE-A 10029338 and JP-A 2000-143244.

The preparation of novel multimetal oxide materials (I) can, however, also be effected by first producing a multimetal oxide material I', which differs from a multimetal oxide material (I)
45 only in that d is 0.

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Such a preferably finely divided multimetal oxide material I' can then be impregnated with solutions (e.g. aqueous solutions) of elements M^3 (e.g. by spraying), then dried (preferably at $\leq 100^\circ\text{C}$) and then calcined (preferably in an inert gas stream) as described above for the precursor multimetal oxides (here, preliminary decomposition in air is preferably dispensed with). The use of aqueous nitrate and/or halide solutions of elements M^3 and/or the use of aqueous solutions in which the elements M^3 are present as a complex with organic compounds (e.g. acetates or acetylacetonates) is particularly advantageous for this preparation variant.

The novel multimetal oxides (I) obtainable as described can be used as such [e.g. as a powder or after pelleting of the powder (frequently with addition of from 0.5 to 2% by weight of finely divided graphite) and subsequent comminution to give chips] or can be shaped into moldings for the novel process. The catalyst bed may be a fixed bed, a moving bed or a fluidized bed.

The shaping to give moldings can be effected, for example, by application to a support, as described in DE-A 10118814 or PCT/EP/02/04073 or DE-A 10051419.

The supports to be used for the multimetal oxide materials (I) to be used according to the invention are preferably chemically inert, i.e. they substantially do not participate in the partial catalytic gas-phase oxidation or ammoxidation of the hydrocarbon (e.g. propane and/or propene to acrylic acid), which is catalyzed by the multimetal oxide materials (I) to be used according to the invention.

According to the invention, particularly suitable materials for the supports are alumina, silica, silicates, such as clay, kaolin, steatite (preferably with a low water-soluble alkali content), pumice, aluminum silicate and magnesium silicate, silicon carbide, zirconium dioxide and thorium dioxide.

The surface of the support may be either smooth or rough. Advantageously, the surface of the support is rough since high surface roughness generally results in greater adhesive strength of the applied coat of active material.

Frequently, the surface roughness R_z of the support is from 5 to 200 μm , often from 20 to 100 μm (determined according to DIN 4768, Sheet 1, using a Hommel Tester for DIN-ISO surface variables, from Hommelwerke, DE).

12

Furthermore, the support material may be porous or nonporous. Expediently, the support material is nonporous (total volume of pores, based on the volume of the support, < 1% by volume).

- 5 The thickness of the active oxide material coat present on the novel coated catalysts is usually from 10 to 1 000 μm . However, it may also be from 50 to 700 μm , from 100 to 600 μm or from 150 to 400 μm . Possible coat thicknesses are also from 10 to 500 μm , from 100 to 500 μm or from 150 to 300 μm .

10

In principle, any geometries of the supports are suitable for the novel process. Their longest dimension is as a rule from 1 to 10 mm. However, spheres or cylinders, in particular hollow cylinders, are preferably used as supports. Advantageous

- 15 diameters for spherical supports are from 1.5 to 4 mm. If cylinders are used as supports, their length is preferably from 2 to 10 mm and their external diameter preferably from 4 to 10 mm. In the case of rings, the wall thickness is moreover usually from 1 to 4 mm. Annular supports suitable according to the invention
20 may also have a length of from 3 to 6 mm, an external diameter of from 4 to 8 mm and a wall thickness of from 1 to 2 mm. However, a support ring geometry of 7 mm x 3 mm x 400 or of 5 mm x 3 mm x 2 mm (external diameter x length x internal diameter) is also possible.

25

The preparation of coated catalysts to be used according to the invention can be effected in the simplest manner by preforming oxide materials of the formula (I) which are to be used according to the invention, converting them into finely divided form and
30 finally applying them to the surface of the support with the aid of a liquid binder. For this purpose, the surface of the support is, in the simplest procedure, moistened with the liquid binder and a coat of the active material is bonded to the moistened surface by bringing it into contact with finely divided active
35 oxide material of the formula (I). Finally, the coated support is dried. Of course, the procedure can be repeated periodically to obtain a greater coat thickness. In this case, the coated parent body becomes the new support, etc.

- 40 The fineness of the catalytically active oxide material of the formula (I) which is to be applied to the surface of the support is of course adapted to the desired coat thickness. For the coat thickness range of from 100 to 500 μm , for example, those active material powders in which at least 50% of the total number of
45 powder particles pass through a sieve of mesh size from 1 to 20 μm and whose numerical fraction of particles having a longest dimension above 50 μm is less than 10% are suitable. As a rule,

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the distribution of the longest dimensions of the powder particles corresponds to a Gaussian distribution as a result of the preparation. Frequently, the particle size distribution is as follows:

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D (μm)	1	1.5	2	3	4	6	8	12	16	24	32
x	80.5	76.3	67.1	53.4	41.6	31.7	23	13.1	10.8	7.7	4
y	19.5	23.7	32.9	46.6	58.4	68.3	77	86.9	89.2	92.3	96

10

D (μm)	48	64	96	128
x	2.1	2	0	0
y	97.9	98	100	100

15

Here:

D = diameter of the particle,

20 x = the percentage of particles whose diameter is $\geq D$;
and

y = the percentage of particles whose diameter is $< D$.

For carrying out the coating method described on an industrial scale, it is advisable, for example, to use the basic method disclosed in DE-A 2909671 and that disclosed in DE-A 10051419, i.e. the supports to be coated are initially taken in a preferably inclined (the angle of inclination is as a rule $\geq 0^\circ$ and $\leq 90^\circ$, in general $\geq 30^\circ$ and $\leq 90^\circ$; the angle of inclination is the angle between the central axis of the rotating container and the horizontal) rotating container (e.g. rotating pan or coating drum). The rotating container conveys the, for example, spherical or cylindrical supports through two metering apparatuses arranged at a certain distance in succession. The first of the two metering apparatuses expediently corresponds to a nozzle (e.g. an atomizer nozzle operated with compressed air), through which the supports rolling in the rotating pan are sprayed with the liquid binder and moistened in a controlled manner. The second metering apparatus is present outside the atomization cone of the liquid binder sprayed in and serves for feeding in the finely divided oxidic active material (e.g. via a vibrating chute or a powder screw). The spherical supports moistened in a controlled manner absorb the active material powder fed in, which is compacted by the rolling movement on the outer surface of the, for example, cylindrical or spherical support to form a cohesive coat.

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If required, the support provided with a base coat in this manner passes again through the spray nozzle in the course of the subsequent revolution and is moistened in a controlled manner thereby, in order to be able to accept a further coat of finely divided oxidic active material in the course of the further movement (intermediate drying is as a rule not required). Finely divided oxidic active material and liquid binder are as a rule fed in continuously and simultaneously.

10 The removal of the liquid binder can be effected after the end of the coating, for example by the action of hot gas, such as N_2 or air. Remarkably, the coating method described results in completely satisfactory adhesion both of the successive coats to one another and of the base coat to the surface of the support.

15 What is important for the coating method described above is that the moistening of the support surface to be coated is carried out in a controlled manner. In short, this means that the support surface is expediently moistened in such a way that, although adsorbed liquid binder is present on it, no liquid phase as such is visible on the support surface. If the support surface is too moist, the finely divided catalytically active oxide material agglomerates to form separate agglomerates instead of being applied to the surface. Detailed information in this context can be found in DE-A 2909671 and in DE-A 10051419.

The abovementioned final removal of the liquid binder used can be carried out in a controlled manner, for example by evaporation and/or sublimation. In the simplest case, this can be effected by the action of hot gases at an appropriate temperature (frequently from 50 to 300°C, often 150°C). However, preliminary drying only can be effected by the action of hot gases. The final drying can then be carried out, for example, in a drying oven of any desired type (e.g. belt dryer) or in the reactor. The temperature applied should not be above the calcination temperature used for the preparation of the oxidic active material. Of course, the drying can also be carried out exclusively in a drying oven.

The following may be used as a binder for the coating process, regardless of the type and geometry of the support: water, monohydric alcohols, such as ethanol, methanol, propanol and butanol, polyhydric alcohols, such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol or glycerol, monobasic or polybasic organic carboxylic acids, such as propionic acid, oxalic acid, malonic acid, glutaric acid or maleic acid, amino alcohols, such as ethanolamine or diethanolamine, and monofunctional or polyfunctional organic amides, such as

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formamide. Advantageous binders are also solutions consisting of from 20 to 90% by weight of water and from 10 to 80% by weight of an organic compound which is dissolved in water and whose boiling point or sublimation temperature at atmospheric pressure (1 atm) is $> 100^{\circ}\text{C}$, preferably $> 150^{\circ}\text{C}$. Advantageously, the organic compound is selected from the above list of possible organic binders. Preferably, the organic proportion of abovementioned aqueous binder solutions is from 10 to 50, particularly preferably from 20 to 30, % by weight. Other suitable organic components are monosaccharides and oligosaccharides, such as glucose, fructose, sucrose or lactose, and polyethylene oxides and polyacrylates.

The fact that the preparation of coated catalysts suitable according to the invention can be carried out not only by application of the prepared, finely milled active oxide materials of the formula (I) to the moistened support surface is important.

Rather, instead of the active oxide material, a finely divided precursor material thereof can also be applied to the moistened support surface (with the use of the same coating methods and binders) and the calcination carried out after drying of the coated support (it is also possible for supports to be impregnated with a precursor solution, then dried and then calcined). Finally, if required, the phases other than the i-phase can be washed out.

A suitable finely divided precursor material of this type is, for example, the material which is obtainable by first producing a very intimate, preferably finely divided, dry blend from the sources of the elemental constituents of the desired active oxide material of the formula (I) (for example by spray drying an aqueous suspension or solution of the sources) and thermally treating this finely divided dry blend (if required, after pelleting with addition of from 0.5 to 2% by weight of finely divided graphite) at from 150 to 350°C , preferably from 250 to 350°C , under an oxidizing (oxygen-containing) atmosphere (e.g. under air) and finally subjecting it, if required, to milling.

After the coating of the supports with the precursor material, calcination is then effected, preferably under an inert gas atmosphere (all other atmospheres are also suitable) at from 360 to 700°C or from 400 to 650°C or from 400 to 600°C .

Of course, the shaping of multimetal oxide materials (I) which can be used according to the invention can also be effected by extrusion and/or pelleting of both finely divided multimetal

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oxide material (I) and finely divided precursor material of a multimetal oxide material (I) (if required, the washing out of the phases other than the i-phase can be carried out at the end).

- 5 Suitable geometries are spheres, solid cylinders and hollow cylinders (rings). The longest dimension of the abovementioned geometries is as a rule from 1 to 10 mm. In the case of cylinders, their length is preferably from 2 to 10 mm and their external diameter preferably from 4 to 10 mm. In the case of
10 rings, the wall thickness is moreover usually from 1 to 4 mm. Annular unsupported catalysts suitable according to the invention can also have a length of from 3 to 6 mm, an external diameter of from 4 to 8 mm and a wall thickness of from 1 to 2 mm. However, unsupported catalyst rings measuring 7 mm x 3 mm x 4 mm or
15 5 mm x 3 mm x 2 mm (external diameter x length x internal diameter) are also possible.

Of course, suitable geometries of the multimetal oxide active materials (I) to be used for the novel process are also all those
20 of DE-A 10101695.

As stated above, it is important according to the invention that the multimetal oxide materials (I) to be used according to the invention have an X-ray diffraction pattern (in this document,
25 always based on $\text{CuK}\alpha$ radiation) which has reflections h, i and k whose peaks are at the diffraction angles (2θ) $22.2 \pm 0.4^\circ$ (h), $27.3 \pm 0.4^\circ$ (i) and $28.2 \pm 0.4^\circ$ (k),

- the reflection h being the one with the strongest intensity
30 within the X-ray diffraction pattern and having an FWHH of not more than 0.5° ,
- the intensity P_i of the reflection i and the intensity P_k of the reflection k satisfying the relationship $0.65 \leq R \leq 0.85$,
35 where R is the intensity ratio defined by the formula

$$R = P_i / (P_i + P_k)$$

and

- 40 — the FWHH of the reflection i and that of the reflection k being each $\leq 1^\circ$.

At the same time, the X-ray diffraction pattern should have no
45 reflection with the peak position $2\theta = 50.0 \pm 0.3^\circ$.

As stated above, the definition of the intensity of a reflection in the X-ray diffraction pattern in this document is based on the definition given in DE-A 19835247, and the definition given in DE-A 10051419 and DE-A 10046672.

5

This means that if A^1 is the peak of a reflection 1 and B^1 is the next pronounced minimum (minima having reflection shoulders are not taken into account), to the left of the peak A^1 in the line of the X-ray diffraction pattern when viewed along the intensity
10 axis perpendicular to the 2θ axis, and B^2 is, in a corresponding manner, the next pronounced minimum to the right of the peak A^1 and C^1 is the point at which a straight line drawn from the peak A^1 perpendicular to the 2θ axis intersects a straight line connecting the points B^1 and B^2 , then the intensity of the
15 reflection 1 is the length of the straight segment A^1C^1 which extends from the peak A^1 to the point C^1 . The expression minimum means a point at which the gradient of a tangent to the curve in a base region of the reflection 1 changes from a negative value to a positive value, or a point at which the gradient tends to
20 zero, the coordinates of the 2θ axis and of the intensity axis being used for determining the gradient.

In this document, the FWHH is, in a corresponding manner, the length of the straight segment between the two points of
25 intersection H^1 and H^2 when the line parallel to the 2θ axis is drawn in the middle of the straight segment A^1C^1 , H^1 , H^2 meaning the first point of intersection of this parallel line in each case with the line of the X-ray diffraction pattern, as defined above, to the left and right of A^1 .

30

An exemplary procedure for determining FWHH and intensity is also shown in figure 6 in DE-A 10046672.

Of course, the multimetal oxide materials (I) to be used
35 according to the invention can also be employed as catalytically active materials in a form diluted with finely divided, e.g. colloidal, materials, such as silica, titanium dioxide, alumina, zirconium oxide or niobium oxide.

40 The dilution mass ratio may be up to 9 (diluent) : 1 (active material), i.e. possible dilution mass ratio are, for example, 6 (diluent) : 1 (active material) and 3 (diluent) : 1 (active material). The incorporation of the diluents can be effected before and/or after the calcination, as a rule even before the
45 drying.

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If the incorporation is effected before the drying or before the calcination, the diluent must be chosen so that it remains substantially unchanged in the fluid medium or during the calcination. This generally occurs, for example, in the case of
5 oxides calcined at appropriately high temperatures.

The novel multimetal oxide materials (I) are suitable as such or in dilute form as described above as active materials for heterogeneously catalyzed partial gas-phase oxidations (including
10 oxydehydrogenations) and/or ammoxidations of saturated and/or unsaturated hydrocarbons.

Such saturated and/or unsaturated hydrocarbons are in particular ethane, ethylene, propane, propylene, n-butane, isobutane and
15 isobutene. Desired products are in particular acrolein, acrylic acid, methacrolein, methacrylic acid, acrylonitrile and methacrylonitrile. However, they are also suitable for the heterogeneously catalyzed partial gas-phase oxidation and/or ammoxidation of compounds such as acrolein and methacrolein.

20

However, ethylene, propylene and acetic acid may also be desired products.

Complete oxidation of the hydrocarbon is understood in this
25 document as meaning that the total amount of carbon contained in the hydrocarbon was converted into oxides of carbon (CO, CO₂).

All reactions of the hydrocarbons under the reactive influence of molecular oxygen which differ therefrom are subsumed in this
30 document by the term partial oxidation. The additional reactive influence of ammonia is a feature of partial ammoxidation.

Novel multimetal oxide materials (I) described in this document are preferably suitable as catalytically active materials for the
35 conversion of propane to acrolein and/or acrylic acid, of propane to acrylic acid and/or acrylonitrile, of propylene to acrolein and/or acrylic acid, of propylene to acrylonitrile, of isobutane to methacrolein and/or methacrylic acid, of isobutane to methacrylic acid and/or methacrylonitrile, of ethane to ethylene,
40 of ethane to acetic acid and of ethylene to acetic acid.

The procedure for such partial oxidations and/or ammoxidations (by the choice of the ammonia content in the reaction mixture, to be controlled in a manner known per se, the reaction can be
45 designed substantially exclusively as a partial oxidation or exclusively as a partial ammoxidation, or as a superposition of the two reactions; cf. for example WO 98/22421) is known per se

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from the i-/k-phase mixed crystal systems of the prior art and can be carried out in a completely corresponding manner.

If the hydrocarbon used is crude propane or crude propylene, this preferably has the composition as described in DE-A 10246119 or DE-A 10118814 or PCT/EP/02/04073. The procedure is preferably also effected as described there.

A partial oxidation of propane to acrylic acid which is to be carried out using catalysts comprising multimetal oxide (I) as active material can be carried out, for example, as described in EP-A 608838, WO 0029106, JP-A 10-36311 and EP-A 1192987.

For example, air, air enriched with oxygen, air depleted in oxygen or pure oxygen can be used as a source of the required molecular oxygen.

Such a process is also advantageous when the reaction gas starting mixture contains no noble gas, in particular no helium, as inert diluent gas. Otherwise, the reaction gas starting mixture can of course comprise inert diluent gases, e.g. N₂, CO and CO₂, in addition to propane and molecular oxygen. Steam as a component of the reaction gas mixture is advantageous according to the invention.

This means that the reaction gas starting mixture with which the novel multimetal oxide material is to be loaded at reaction temperatures of, for example, from 200 to 550°C or from 230 to 480°C or from 300 to 440°C and pressures of from 1 to 10 or from 2 to 5 bar may have, for example, the following composition:

from 1 to 15, preferably from 1 to 7, % by volume of propane,
from 44 to 99% by volume of air and
from 0 to 55% by volume of steam.

Steam-containing reaction gas starting mixtures are preferred.

The following are suitable as other possible compositions of the reaction gas starting mixture:

from 70 to 95% by volume of propane,
from 5 to 30% by volume of molecular oxygen and
from 0 to 25% by volume of steam.

20

In such a process, a product gas mixture which does not consist exclusively of acrylic acid is of course obtained. Rather, the product gas mixture contains, in addition to unconverted propane, secondary components such as propene, acrolein, CO₂, CO, H₂O, 5 acetic acid, propionic acid, etc., from which the acrylic acid has to be separated off.

This can be effected in the manner known from the heterogeneously catalyzed gas-phase oxidation of propene to acrylic acid.

10

This means that the acrylic acid present can be taken up from the product gas mixture by absorption with water or by absorption with a high-boiling inert hydrophobic organic solvent (for example, a mixture of diphenyl ether and diphenyl, which, if

15 required, may also contain additives such as dimethyl phthalate).

The resulting mixture of absorbent and acrylic acid can then be worked up by rectification, extraction and/or crystallization in a manner known per se to give the pure acrylic acid.

Alternatively, the basic separation of the acrylic acid from the

20 product gas mixture can also be effected by fractional condensation, as described, for example, in DE-A 19 924 532.

The resulting aqueous acrylic acid condensate can then be further purified, for example by fractional crystallization (e.g.

25 suspension crystallization and/or layer crystallization).

The residual gas mixture remaining in the basic separation of the acrylic acid contains in particular unconverted propane, which is preferably recycled to the gas-phase oxidation. For this purpose,

30 it can be partly or completely separated from the residual gas mixture, for example by fractional rectification under superatmospheric pressure, and then recycled to the gas-phase oxidation. However, it is more advantageous to bring the residual gas into contact, in an extraction apparatus, with a hydrophobic 35 organic solvent (e.g. by passing the latter through) which is capable of absorbing propane.

By subsequent desorption and/or stripping with air, the absorbed propane can be liberated again and can be recycled to the novel

40 process. In this way, economical total propane conversions can be achieved. As in other separation processes, propene formed as a secondary component is as a rule not separated or not completely separated from the propane and is circulated with the latter.

This also applies in the case of other homologous saturated and

45 olefinic hydrocarbons. In particular, it applies very generally

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for novel heterogeneously catalyzed partial oxidations and/or ammoxidations of saturated hydrocarbons.

It is advantageous that the novel multimetal oxide materials are also capable of heterogeneously catalyzing the partial oxidation and/or ammoxidation of the homologous olefinic hydrocarbon to the same desired product.

Thus, using the novel multimetal oxide materials (I) as active materials, acrylic acid can be prepared by heterogeneously catalyzed partial gas-phase oxidation of propene with molecular oxygen, as described in DE-A 10118814 or PCT/EP/02/04073 or JP-A 7-53448.

- 15 This means that a single reaction zone A is sufficient for carrying out the novel process. Exclusively catalysts comprising multimetal oxide materials (I) are present as catalytically active materials in this reaction zone.
- 20 This is unusual since the heterogeneously catalyzed gas-phase oxidation of propene to acrylic acid takes place very generally in two steps effected in succession in terms of time. In the first step, usually propene is substantially oxidized to acrolein and, in the second step, usually acrolein formed in the first
- 25 step is oxidized to acrylic acid.

Conventional processes for the heterogeneously catalyzed gas-phase oxidation of propene to acrylic acid therefore usually use a special catalyst type tailored to the oxidation step for

30 each of the two abovementioned oxidation steps.

This means that the conventional processes for the heterogeneously catalyzed gas-phase oxidation of propene to acrylic acid operate with two reaction zones, in contrast to the

35 novel process.

In the novel process for the partial oxidation of propene in the one reaction zone A, it is of course possible for only one or more than one catalyst comprising multimetal oxide materials (I)

40 to be present. Of course, the catalysts to be used according to the invention can be diluted with inert material, as was recommended in this document, for example, also as support material.

45 In the novel process for the partial oxidation of propene, it is possible for only one temperature or a temperature changing along the reaction zone A to prevail along the one reaction zone A,

22

said temperature being produced by a heating medium for heating the reaction zone. This temperature change may then increase or decrease.

5 If the novel process for the partial oxidation of propene is carried out as a fixed-bed oxidation, it is expediently carried out in a tube-bundle reactor whose catalyst tubes are loaded with the catalyst. Usually, a liquid, as a rule a salt bath, is passed as a heating medium around the catalyst tubes.

10

A plurality of temperature zones along the reaction zone A can then be realized in a simple manner if more than one salt bath is passed around the catalyst tubes segment by segment along the catalyst tubes.

15

When considered over the reactor, the reaction gas mixture in the catalyst tubes is fed either cocurrent with or countercurrent to the salt bath. The salt bath itself can execute purely parallel flow relative to the catalyst tubes. However, a transverse flow

20 can of course also be superposed on said parallel flow. Overall, the salt bath can also execute, around the catalyst tubes, a meandering flow which is cocurrent with or countercurrent to the reaction gas mixture only when considered over the reactor.

25 In the novel process for the partial oxidation of propene of the partial oxidation of propane, the reaction temperature may be from 200 to 500°C along the total reaction zone A. Usually, it is from 250 to 450°C. Preferably, the reaction temperature is from 330 to 420°C, particularly preferably from 350 to 400°C.

30

In the novel process for the partial oxidation of propene, the operating pressure may be 1 bar, less than 1 bar or more than 1 bar. Operating pressures typical according to the invention are from 1.5 to 10, frequently from 1.5 to 5, bar.

35

The propene to be used for the novel process for the partial oxidation of propene does not have to meet any particularly high requirements with respect to its purity.

40 As stated above and as is true very generally for all one- or two-stage processes for the heterogeneously catalyzed gas-phase oxidation of propene to acrolein and/or acrylic acid, for example propene (also referred to as crude propene) having the following two specifications can be used entirely without problems as

45 propene for such a process:

23

a) Polymer-grade propylene:

5	$\geq 99.6\%$ by weight	Propene,
	$\leq 0.4\%$ by weight	Propane,
	≤ 300 ppm by weight	Ethane and/or methane,
10	≤ 5 ppm by weight	C ₄ -hydrocarbons,
	≤ 1 ppm by weight	Acetylene,
	≤ 7 ppm by weight	Ethylene,
15	≤ 5 ppm by weight	Water,
	≤ 2 ppm by weight	O ₂ ,
	≤ 2 ppm by weight	Sulfur-containing compounds (calculated as sulfur),
20	≤ 1 ppm by weight	Chlorine-containing compounds (calculated as chlorine),
	≤ 5 ppm by weight	CO ₂ ,
	≤ 5 ppm by weight	CO,
25	≤ 10 ppm by weight	Cyclopropane,
	≤ 5 ppm by weight	Propadiene and/or propyne,
	≤ 10 ppm by weight	C ₂₅ -hydrocarbons and
30	≤ 10 ppm by weight	Carbonyl-containing compounds (calculated as Ni(CO) ₄).

35

b) Chemical-grade propylene:

40	$\geq 94\%$ by weight	Propene,
	$\leq 6\%$ by weight	Propane,
	$\leq 0.2\%$ by weight	Methane and/or ethane,
45	≤ 5 ppm by weight	Ethylene,
	≤ 1 ppm by weight	Acetylene,
	≤ 20 ppm by weight	Propadiene and/or propyne,

5	≤ 100 ppm by weight	Cyclopropane,
	≤ 50 ppm by weight	Butene,
	≤ 50 ppm by weight	Butadiene,
	≤ 200 ppm by weight	C ₄ -hydrocarbons,
	≤ 10 ppm by weight	C ₂₅ -hydrocarbons,
10	≤ 2 ppm by weight	Sulfur-containing compounds (calculated as sulfur),
	≤ 0.1 ppm by weight	Sulfides (calculated as H ₂ S),
	≤ 1 ppm by weight	Chlorine-containing compounds (calculated as chlorine),
15	≤ 0.1 ppm by weight	Chlorides (calculated as Cl [⊖]) and
	≤ 30 ppm by weight	Water.

Of course, all abovementioned possible impurities in the propene can however each also be present in from two to ten times the stated individual amount in the crude propene without the usability of the crude propene for the novel process or for the known processes for the one- or two-stage heterogeneously catalyzed gas-phase oxidation of propene to acrolein and/or acrylic acid very generally being adversely affected.

This applies in particular when the saturated hydrocarbons, the steam, the oxides of carbon and the molecular oxygen are compounds which participate either as inert diluent gases or as reactants in large amounts in the reaction in the abovementioned process. Usually, the crude propene as such is mixed with recycle gas, air and/or molecular oxygen and/or dilute air and/or inert gas before being used for the novel process and all other processes of the heterogeneously catalyzed gas-phase oxidation of propene to acrolein and/or acrylic acid.

However, another suitable propene source for the novel process is propene which is formed as a byproduct in a process other than the novel process and contains, for example, up to 40% by weight of propane. This propene may additionally be accompanied by other impurities which substantially do not interfere with the novel process.

25

Both pure oxygen and air or air enriched with or depleted in oxygen can be used as an oxygen source for the novel process for the partial oxidation of propene.

- 5 In addition to molecular oxygen and propene, the reaction gas starting mixture to be used for the novel process usually also contains at least one diluent gas. Suitable diluent gases are nitrogen, oxides of carbon, noble gases and lower hydrocarbons, such as methane, ethane and propane (higher hydrocarbons, e.g. C₄-hydrocarbons, should be avoided). Frequently, steam is also used as a diluent gas. Often, mixtures of abovementioned gases form the diluent gas for the novel process for the partial oxidation of propene.
- 10
- 15 According to the invention, the novel heterogeneously catalyzed oxidation of propene is advantageously effected in the presence of propane.

- Typically, the reaction gas starting mixture for the novel process has the following composition (molar ratios):
- 20

Propene : oxygen : H₂O : other diluent gases
= 1 : (0.1 - 10) : (0 - 70) : (0 : 20).

- 25 The abovementioned ratio is preferably 1 : (1 - 5) : (1 - 40) : (0 - 10).

- If propane is used as diluent gas, it can, as described, advantageously likewise be partly oxidized to acrylic acid in the novel process.
- 30

According to the invention, the reaction gas starting mixture advantageously contains molecular oxygen, CO, CO₂, steam and propane as diluent gas.

35

The molar propane : propene ratio in the novel process may assume the following values: from 0 to 15, frequently from 0 to 10, often from 0 to 5, expediently from 0.01 to 3.

- 40 The loading of the catalyst bed with propene in the novel process for the partial oxidation of propene is, for example, from 40 to 250 l(S.T.P.)/l.h. The loading with reaction gas starting mixture is frequently from 500 to 15 000, often from 600 to 10 000, frequently from 700 to 5 000, l(S.T.P.)/l.h.

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In the novel process for the partial oxidation of propene to acrylic acid, the product gas mixture obtained does not of course consist exclusively of acrylic acid. Rather, the product gas mixture contains, in addition to unconverted propene, secondary components such as propane, acrolein, CO₂, CO, H₂O, acetic acid, propionic acid, etc., from which the acrylic acid has to be separated off.

This can be effected in a manner known generally from the heterogeneously catalyzed two-stage gas-phase oxidation (carried out in two reaction zones) of propene to acrylic acid.

This means that the acrylic acid present can be taken up from the product gas mixture by absorption with water or by absorption with a high-boiling inert hydrophobic organic solvent (for example, a mixture of diphenyl ether and diphenyl, which, if required, may also contain additives such as dimethyl phthalate). The resulting mixture of absorbent and acrylic acid can then be worked up by rectification, extraction and/or crystallization in a manner known per se to give the pure acrylic acid. Alternatively, the basic separation of the acrylic acid from the product gas mixture can also be effected by fractional condensation, as described, for example, in DE-A 19 924 532.

The resulting aqueous acrylic acid condensate can then be further purified, for example, by fractional crystallization (e.g. suspension crystallization and/or layer crystallization).

The residual gas mixture remaining in the basic separation of acrylic acid contains in particular unconverted propene (and may contain propane). This can be separated from the residual gas mixture, for example by fractional rectification under superatmospheric pressure, and then recycled to the novel gas-phase oxidation. However, it is more advantageous to bring the residual gas into contact, in an extraction apparatus, with a hydrophobic organic solvent (e.g. by passing the latter through) which is capable of preferentially absorbing the propene (and any propane).

By subsequent desorption and/or stripping with air, the absorbed propene (and any propane) can be liberated again and recycled to the novel process. In this way, economical overall propene conversions can be achieved. If propene is subjected to partial oxidation in the presence of propane, propene and propane are preferably separated off and recycled together.

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In a completely corresponding manner, the novel multimetal oxides (I) can be used as catalysts for the partial oxidation of isobutane and/or isobutene to methacrylic acid.

- 5 Their use for the ammoxidation of propane and/or propene can be effected, for example, as described in EP-A 529853, DE-A 2351151, JP-A 6-166668 and JP-A 7-232071.

- 10 Their use for the ammoxidation of n-butane and/or n-butene can be effected as described in JP-A 6-211767.

Their use for the oxydehydrogenation of ethane to ethylene or the further reaction to acetic acid can be effected as described in US-A 4250346 or as described in EP-B 261264.

15

The novel multimetal oxide materials (I) can, however, also be integrated in other multimetal oxide materials (for example, their finely divided materials can be mixed, if required compressed and calcined or can be mixed as sludges (preferably

- 20 aqueous), dried and calcined (for example as described in EP-A 529853 for multimetal oxide materials (I) with $d = 0$)). Preferably, once again calcination is effected under inert gas.

- The resulting multimetal oxide materials (referred to below as overall materials) preferably contain ≥ 50 , particularly preferably ≥ 75 , very particularly preferably ≥ 90 or ≥ 95 , % by weight of multimetal oxide materials (I) and are likewise suitable for the partial oxidations and/or ammoxidations discussed in this document.

30

The overall materials also preferably have no reflection peak position at $2\theta = 50.0 \pm 3.0^\circ$.

- 35 If the overall material has a reflection peak position at $2\theta = 50.0 \pm 3.0^\circ$, it is advantageous if the amount by weight of the multimetal oxide materials (I) is ≥ 80 or ≥ 90 or $\geq 95\%$ by weight. Such overall materials are obtainable, for example, by not washing out quantitatively in the novel preparation process for the multimetal oxide materials (I).

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The geometric shaping is expediently effected in the case of the overall materials as described for the multimetal oxide materials (I).

- 45 The advantageousness of the novel multimetal oxide materials (I) is based on their excellent selectivity with respect to the desired product. It is surprising that the promoters M^3 are also

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effective in pure i-phase, in particular with regard to both the partial oxidations mentioned in the document and partial ammoxidations.

- 5 For the purpose of the heterogeneously catalyzed partial gas-phase oxidation of propane to acrylic acid, the novel multimetal oxide materials (I) and multimetal oxide materials or catalysts containing them are preferably put into operation as described in DE-A 10122027.

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Examples

- A) Preparation of coated catalysts comprising multimetal oxide materials

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Comparative example 1 (preparation of a multimetal oxide catalyst comprising the active material $\text{Mo}_{1.0}\text{V}_{0.33}\text{Te}_{0.19}\text{Nb}_{0.11}\text{Ni}_{0.01}\text{O}_x$, containing i- and k-phases)

- 20 87.61 g of ammonium metavanadate (78.55% by weight of V_2O_5 , from G.f.E. Nürnberg, DE) were dissolved at 80°C in 3 040 ml of water (three-necked flask with stirrer, thermometer, reflux condenser and heating) while stirring. A clear, yellowish solution formed. This solution was cooled to 60°C and then, while maintaining the
- 25 60°C, 117.03 g of telluric acid (99% by weight of H_6TeO_6 , from Aldrich) and 400.00 g of ammonium heptamolybdate (82.52% by weight of MoO_3 , from Starck/Goslar) were stirred in succession in the stated sequence into the solution. The resulting deep red solution was cooled to 30°C and then, while maintaining the 30°C,
- 30 25.60 g of an aqueous solution of 6.80 g of nickel(II) nitrate hexahydrate (98% by weight, from Fluka) in 20 g of water (dissolution was effected at 25°C) were added. The solution A which was at 30°C was thus obtained.
- 35 Separately therefrom, 112.67 g of ammonium niobium oxolate (20.8% by weight of Nb, from Starck/Goslar) were dissolved at 60°C in 500 ml of water in a beaker to give a solution B. Solution B was cooled to 30°C and was combined at this temperature with the solution A having the same temperature, solution B being added to
- 40 solution A. The addition was effected continuously over a period of 5 min. An orange suspension formed.

This suspension was then spray-dried in a spray dryer from Niro (Niro A/S Atomizer, Transportable Minor unit, centrifugal

- 45 atomizer from Niro, DK). The temperature of the initially taken mixture was 30°C. The gas entry temperature T_{in} was 320°C and the

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gas exit temperature T_{out} was 110°C. The resulting spray-dried powder was likewise orange.

100 g of the spray-dried powder were heated in a rotating bulb
oven according to figure 1 (quartz glass bulb having an internal
volume of 1 liter; 1 = oven housing, 2 = rotating flask, 3 =
heated space, 4 = nitrogen/air stream) under a stream of 50
l(S.T.P.)/h of air in the course of 27.5 minutes, initially
heated linearly from 25°C to 275°C, and this temperature and the
air stream were then maintained for 1 hour. Immediately
thereafter, the air stream was replaced by a stream of
50 l(S.T.P.)/h of nitrogen and heating was effected linearly from
275°C to 600°C in the course of 32.5 minutes. This temperature and
the nitrogen stream were then maintained for 2 hours. Finally,
the entire rotating-bulb oven was cooled to 25°C while maintaining
the nitrogen stream.

A black powder having the composition $Mo_{1.0}V_{0.33}Te_{0.19}Nb_{0.11}Ni_{0.01}O_x$
(stoichiometry of weighed in materials:
 $Mo_{1.0}V_{0.33}Te_{0.22}Nb_{0.11}Ni_{0.01}O_x$) was obtained. The associated X-ray
diffraction pattern is shown in figure 2 ($R = 0.26$). BET =
8.0 m²/g.

The active material powder was then milled in a Retsch mill
(centrifugal mill, type ZM 100, from Retsch, DE) (particle size
≤ 0.12 mm).

38 g of the powder present after milling was applied to 150 g of
spherical supports having a diameter of from 2.2 to 3.2 mm ($R_z =$
45 μm, support material = steatite from Ceramtec, DE, total pore
volume of the support ≤ 1% by volume, based on the total support
volume). For this purpose, the support was initially taken in a
coating drum having an internal volume of 2 l (angle of
inclination of the central axis of the drum relative to the
horizontal = 30°). The drum was rotated at 25 revolutions per
minute. About 25 ml of a mixture of glycerol and water
(glycerol:water weight ratio = 1:3) were sprayed onto the support
for 60 minutes via an atomizer nozzle operated with
300 l(S.T.P.)/h of compressed air. The nozzle was installed in
such a way that the spray cone wetted the supports conveyed in
the drum by lifting plates to the uppermost point of the inclined
drum, in the upper half of the rolling zone. The finely divided
active material powder was introduced into the drum via a powder
screw, the point of addition of the powder being within the
rolling zone or below the spray cone. By a periodic repetition of

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the wetting and powder metering, the support provided with a base coat itself became the support in the subsequent period.

After completion of coating, the coated support was dried under
5 air for 16 hours at 150°C in a muffle furnace. A coated catalyst CE1 comprising 20% by weight of active material resulted.

Example 1

- 10 As for comparative example 1. However, the powder resulting after milling in the Retsch mill was stirred under reflux in 1 000 ml of a 10% strength by weight HNO₃ solution for 7 hours at 70°C. The remaining solid was filtered off from the resulting suspension and washed nitrate-free with water. The filter cake was then
15 dried overnight under air at 110°C in a muffle furnace.

The resulting active material had the composition Mo_{1.0}V_{0.29}Te_{0.14}Nb_{0.13}Ni_{0.007}O_x. The associated X-ray diffraction pattern is shown in figure 3 (R = 0.71). BET = 20.2 m²/g.

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It was applied in the same way to the same support as in comparative example 1, so that a coated catalyst E1 comprising 20% by weight of active material resulted.

25 Comparative example 2

As for comparative example 1, but 6.17 g of palladium(II) nitrate dihydrate (98%, from Fluka) were used instead of 6.80 g of nickel(II) nitrate hexahydrate.

30

The resulting active material had the composition Mo_{1.0}V_{0.33}Te_{0.19}Nb_{0.11}Pd_{0.01}O_x. The associated X-ray diffraction pattern is shown in figure 4 (R = 0.25). BET = 9.3 m²/g. It was applied in the same manner to the same support as in comparative
35 example 1, so that a coated catalyst CE2 comprising 20% by weight of active material resulted.

Example 2

- 40 As for example 1, but the active material from comparative example 2 was washed with aqueous nitric acid. The resulting active material had the composition Mo_{1.0}V_{0.28}Te_{0.13}Nb_{0.13}Pd_{0.001}O_x.

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The associated X-ray diffraction pattern is shown in figure 5 ($R = 0.73$). $BET = 22.5 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst E2 comprising 20% by weight of active material resulted.

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Comparative example 3

As for comparative example 1, but the amount of the batch was halved and 12.34 g of palladium(II) nitrate dihydrate (98%, from
10 Fluka) were used instead of 3.40 g of nickel(II) nitrate hexahydrate.

The resulting active material had the composition $\text{Mo}_{1.0}\text{V}_{0.33}\text{Te}_{0.22}\text{Nb}_{0.11}\text{Pd}_{0.04}\text{O}_x$. The associated X-ray diffraction
15 pattern is shown in figure 6 ($R = 0.35$). $BET = 9.3 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst CE3 comprising 20% by weight of active material resulted.

20 Example 3

As for example 1, but the active material from comparative example 3 was washed with aqueous nitric acid. The resulting active material had the composition $\text{Mo}_{1.0}\text{V}_{0.29}\text{Te}_{0.13}\text{Nb}_{0.13}\text{Pd}_{0.001}\text{O}_x$.
25 The associated X-ray diffraction pattern is shown in figure 7 ($R = 0.74$). $BET = 17.4 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst E2 comprising 20% by weight of active material resulted.

30 Comparative example 4

As for comparative example 1, but 3.41 g of cobalt(II) nitrate hexahydrate (98%, from Riedel-de-Haen) were used instead of
6.80 g of nickel(II) nitrate hexahydrate.

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The resulting active material had the composition $\text{Mo}_{1.0}\text{V}_{0.33}\text{Te}_{0.19}\text{Nb}_{0.11}\text{Co}_{0.005}\text{O}_x$. The associated X-ray diffraction pattern is shown in figure 8 ($R = 0.24$). $BET = 8.9 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative
40 example 1, so that a coated catalyst CE4 comprising 20% by weight of active material resulted.

Example 4

45 As for example 1, but the active material from comparative example 4 was washed with aqueous nitric acid.

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The resulting active material had the composition $\text{Mo}_{1.0}\text{V}_{0.29}\text{Te}_{0.13}\text{Nb}_{0.13}\text{Co}_{0.004}\text{O}_x$. The associated X-ray diffraction pattern is shown in figure 9 ($R = 0.73$). $\text{BET} = 24.6 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst E4 comprising 20% by weight of active material resulted.

Comparative example 5

- 10 As for comparative example 1, but 5.65 g of copper(II) nitrate trihydrate (98%, from Acros Organics) were used instead of 6.80 g of nickel(II) nitrate hexahydrate.

The resulting active material had the composition

- 15 $\text{Mo}_{1.0}\text{V}_{0.33}\text{Te}_{0.19}\text{Nb}_{0.11}\text{Cu}_{0.01}\text{O}_x$. The associated X-ray diffraction pattern is shown in figure 10 ($R = 0.27$). $\text{BET} = 6.7 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst CE5 comprising 20% by weight of active material resulted.

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Example 5

As for example 1, but the active material from comparative example 5 was washed with aqueous nitric acid.

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The resulting active material had the composition

- 30 $\text{Mo}_{1.0}\text{V}_{0.28}\text{Te}_{0.13}\text{Nb}_{0.13}\text{Cu}_{0.003}\text{O}_x$. The associated X-ray diffraction pattern is shown in figure 11 ($R = 0.74$). $\text{BET} = 23.1 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst E5 comprising 20% by weight of active material resulted.

Comparative example 6

- 35 As for comparative example 1, but 5.68 g of bismuth(III) nitrate pentahydrate (98.5%, from Merck) were used instead of 6.80 g of nickel(II) nitrate hexahydrate.

The resulting active material had the composition

- 40 $\text{Mo}_{1.0}\text{V}_{0.33}\text{Te}_{0.19}\text{Nb}_{0.11}\text{Bi}_{0.004}\text{O}_x$. The associated X-ray diffraction pattern is shown in figure 12 ($R = 0.18$). $\text{BET} = 9.0 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst CE6 comprising 20% by weight of active material resulted.

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Example 6

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As for example 1, but the active material from comparative example 6 was washed with aqueous nitric acid. The resulting active material had the composition $\text{Mo}_{1.0}\text{V}_{0.28}\text{Te}_{0.15}\text{Nb}_{0.14}\text{Bi}_{0.005}\text{O}_x$. The associated X-ray diffraction pattern is shown in figure 13 ($R = 0.70$). BET = 22.0 m²/g. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst E6 comprising 20% by weight of active material resulted.

Comparative example 7

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As for comparative example 1, but 3.84 g of lead(II) nitrate (Riedel-de-Haen, 99%) were used instead of 6.80 g of nickel(II) nitrate hexahydrate.

15 The resulting active material had the composition

$\text{Mo}_{1.0}\text{V}_{0.34}\text{Te}_{0.18}\text{Nb}_{0.11}\text{Pb}_{0.004}$. The associated X-ray diffraction pattern is shown in figure 14 ($R = 0.30$). BET = 2.2 m²/g. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst CE7 comprising 20% by weight

20 of active material resulted.

Example 7

As for example 1, but the active material from comparative example 7 was washed with aqueous nitric acid. The resulting active material had the composition $\text{Mo}_{1.0}\text{V}_{0.28}\text{Te}_{0.13}\text{Nb}_{0.13}\text{Pb}_{0.001}\text{O}_x$.

The associated X-ray diffraction pattern is shown in figure 15 ($R = 0.67$). BET = 27.1 m²/g. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst E7 comprising 20% by weight of active material resulted.

Comparative example 8

As for comparative example 1, but with the difference that the addition of the 5.60 g of nickel(II) nitrate hexahydrate was not carried out. The resulting active material had the composition $\text{Mo}_{1.0}\text{V}_{0.33}\text{Te}_{0.16}\text{Nb}_{0.11}\text{O}_x$. The associated X-ray diffraction pattern is shown in figure 16 ($R = 0.26$). BET = 6.7 m²/g. It was applied in the same manner to the same support as in comparative example 1, so that a coated catalyst CE7 comprising 20% by weight of active material resulted.

Comparative example 9

As for example 1, but the active material from comparative example 7 was washed with aqueous nitric acid. The resulting 5 active material had the composition $\text{Mo}_{1.0}\text{V}_{0.29}\text{Te}_{0.13}\text{Nb}_{0.13}\text{O}_x$.

The associated X-ray diffraction pattern is shown in figure 17 ($R = 0.68$). $\text{BET} = 26.0 \text{ m}^2/\text{g}$. It was applied in the same manner to the same support as in comparative example 1, so that a coated 10 catalyst CE8 comprising 20% by weight of active material resulted.

B) Testing of the coated catalysts prepared in A) and comprising multimetal oxide materials

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A steel tubular reactor (internal diameter: 8.5 mm, length: 140 cm, wall thickness: 2.5 cm) was loaded with in each case 35.0 g of the respective coated catalyst from A) (catalyst bed length in all cases about 53 cm). A preliminary bed of 30 cm of 20 steatite beads (diameter: from 2.2 to 3.2 mm, manufacturer: Ceramtec) was installed before the catalyst bed and a subsequent bed of the same steatite beads was installed after the catalyst bed, over the remaining length of the tubular reactor.

25 The external temperature of the loaded reaction tube was brought to 350°C over the total length from the outside by means of electrically heated heating mats.

The reaction tube was then fed with a reaction gas starting 30 mixture having the molar composition propane:air: $\text{H}_2\text{O} = 1:15:14$ (the entry side was on the side of the subsequent bed). The residence time (based on the catalyst bed volume) was set at 2.4 seconds. The entry pressure was 2 bar absolute.

35 The feeding of the reaction tube was first started in each case at the abovementioned external temperature of the loaded reaction tube over a period of 24 hours before this external temperature was increased so that, based on a single pass through the reaction tube, a propane conversion (U_{PAN}) of about 78 mol% 40 resulted in all cases.

The table below shows the external temperature T ($^\circ\text{C}$) required for this conversion, as a function of the coated catalyst used, and the resulting selectivity of the acrylic acid formation (S_{ACA} 45 (mol%)) and the selectivity of the propene byproduct formation

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(SPEN (mol%)). In addition, the table shows the intensity ratio R of the active material present on the coated catalyst and the composition of this active material.

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Table

Example	Composition	R	T [°C]	U _{PAN} (mol%)	S _{ACA} (mol%)	S _{PEN} (mol%)
CE1	Mo ₁ V _{0.33} Te _{0.22} Nb _{0.11} Ni _{0.01}	0.26	390	30	66	9
E1	Mo ₁ V _{0.29} Te _{0.14} Nb _{0.13} Ni _{0.007}	0.71	390	80	66	2
CE2	Mo ₁ V _{0.33} Te _{0.19} Nb _{0.11} Pd _{0.01}	0.25	390	80	62	1
E2	Mo ₁ V _{0.28} Te _{0.13} Nb _{0.13} Pd _{0.001}	0.73	420	77	59	1
CE3	Mo ₁ V _{0.33} Te _{0.22} Nb _{0.11} Pd _{0.04}	0.35	440	75	42	1
E3	Mo ₁ V _{0.29} Te _{0.13} Nb _{0.13} Pd _{0.001}	0.74	385	77	60	1
CE4	Mo ₁ V _{0.33} Te _{0.19} Nb _{0.11} Co _{0.005}	0.24	440	79	44	1
E4	Mo ₁ V _{0.29} Te _{0.13} Nb _{0.13} Co _{0.004}	0.73	390	76	62	2
CE5	Mo ₁ V _{0.33} Te _{0.19} Nb _{0.11} Cu _{0.01}	0.27	420	59	56	3
E5	Mo ₁ V _{0.28} Te _{0.13} Nb _{0.13} Cu _{0.003}	0.74	420	73	62	2
CE6	Mo ₁ V _{0.33} Te _{0.19} Nb _{0.11} Bi _{0.004}	0.18	400	83	54	1
E6	Mo ₁ V _{0.28} Te _{0.15} Nb _{0.14} Bi _{0.005}	0.70	410	77	62	1
CE7	Mo ₁ V _{0.34} Te _{0.18} Nb _{0.11} Pb _{0.004}	0.30	440	78	43	1
E7	Mo ₁ V _{0.28} Te _{0.13} Nb _{0.13} Pb _{0.001}	0.67	420	78	58	2
CE8	Mo ₁ V _{0.33} Te _{0.16} Nb _{0.11}	0.26	420	68	55	2
CE9	Mo ₁ V _{0.29} Te _{0.13} Nb _{0.13}	0.68	410	80	56	2

Multimetal oxide material

Abstract

5

A multimetal oxide material contains the elements Mo, V and Te and/or Sb and at least one of the elements Nb, Ti, W, Ta and Ce and promoters and has a specific X-ray diffraction pattern. In addition, such a multimetal oxide material is used as a catalyst for heterogeneously catalyzed gas-phase partial oxidations of hydrocarbons.

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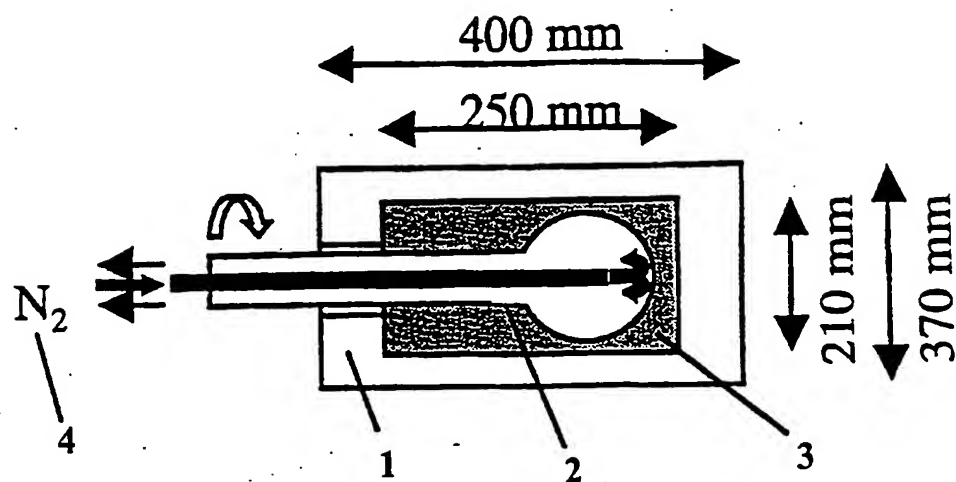


Fig. 1

Fig. 2

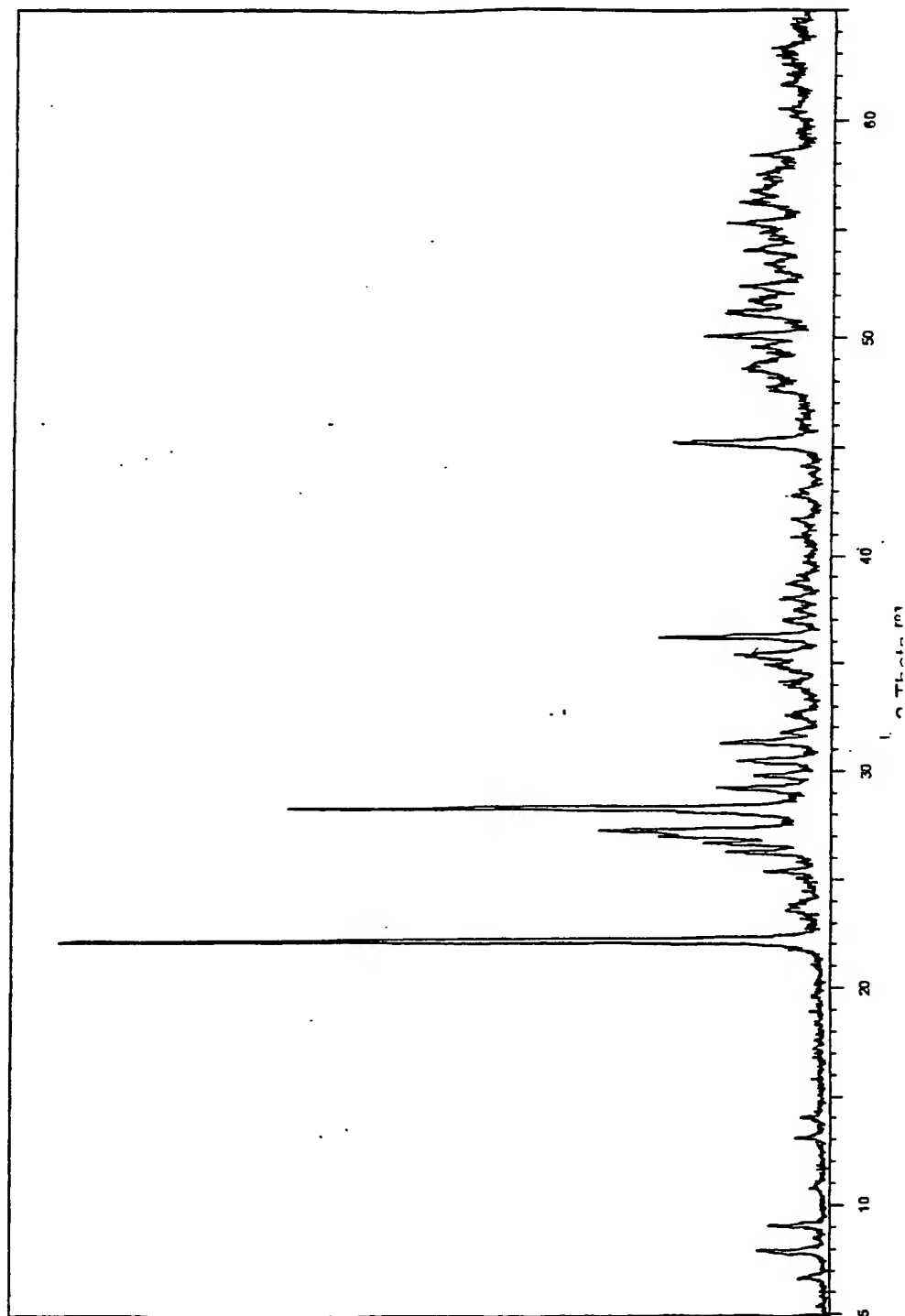


Fig. 3

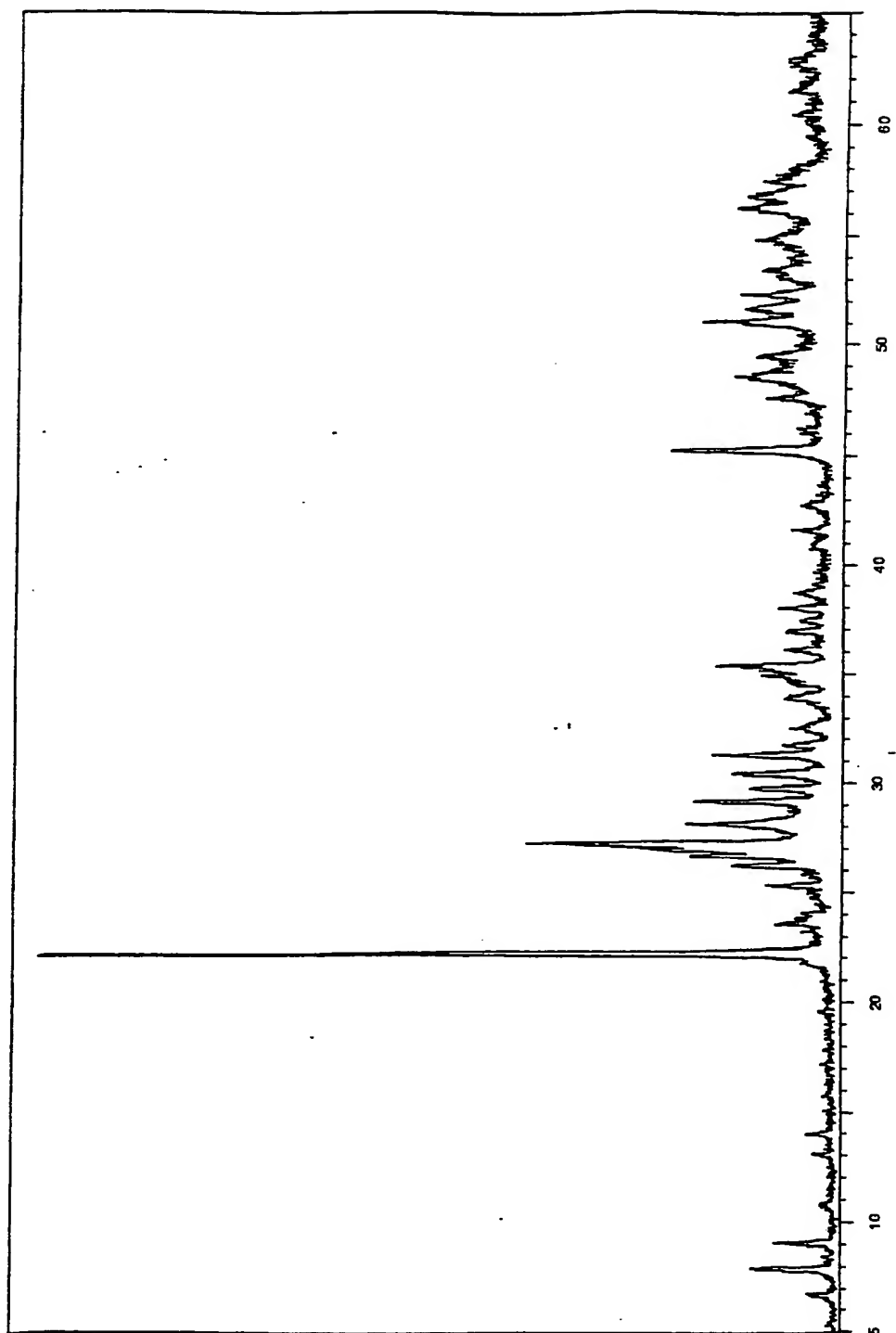


Fig. 4

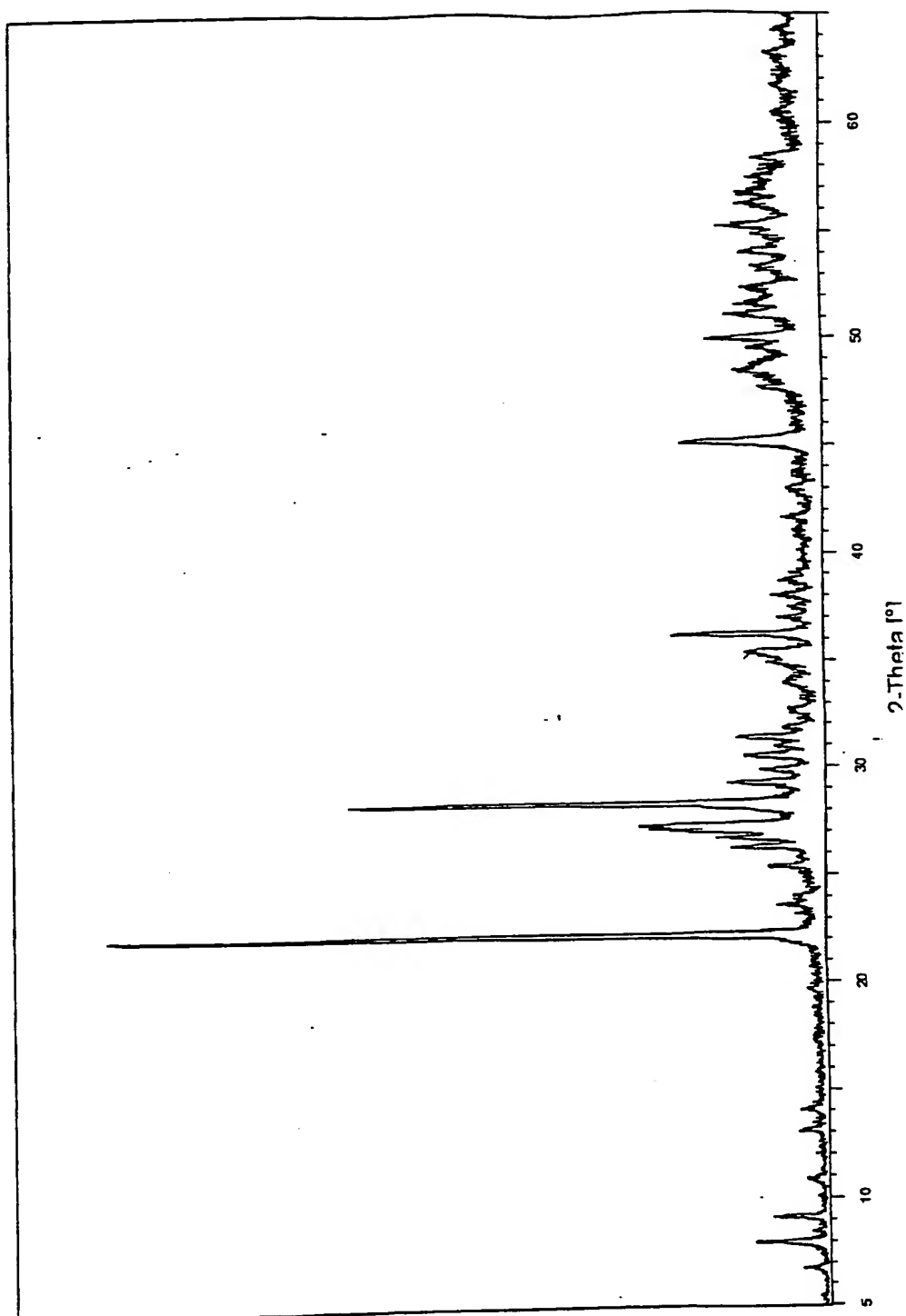


Fig. 5

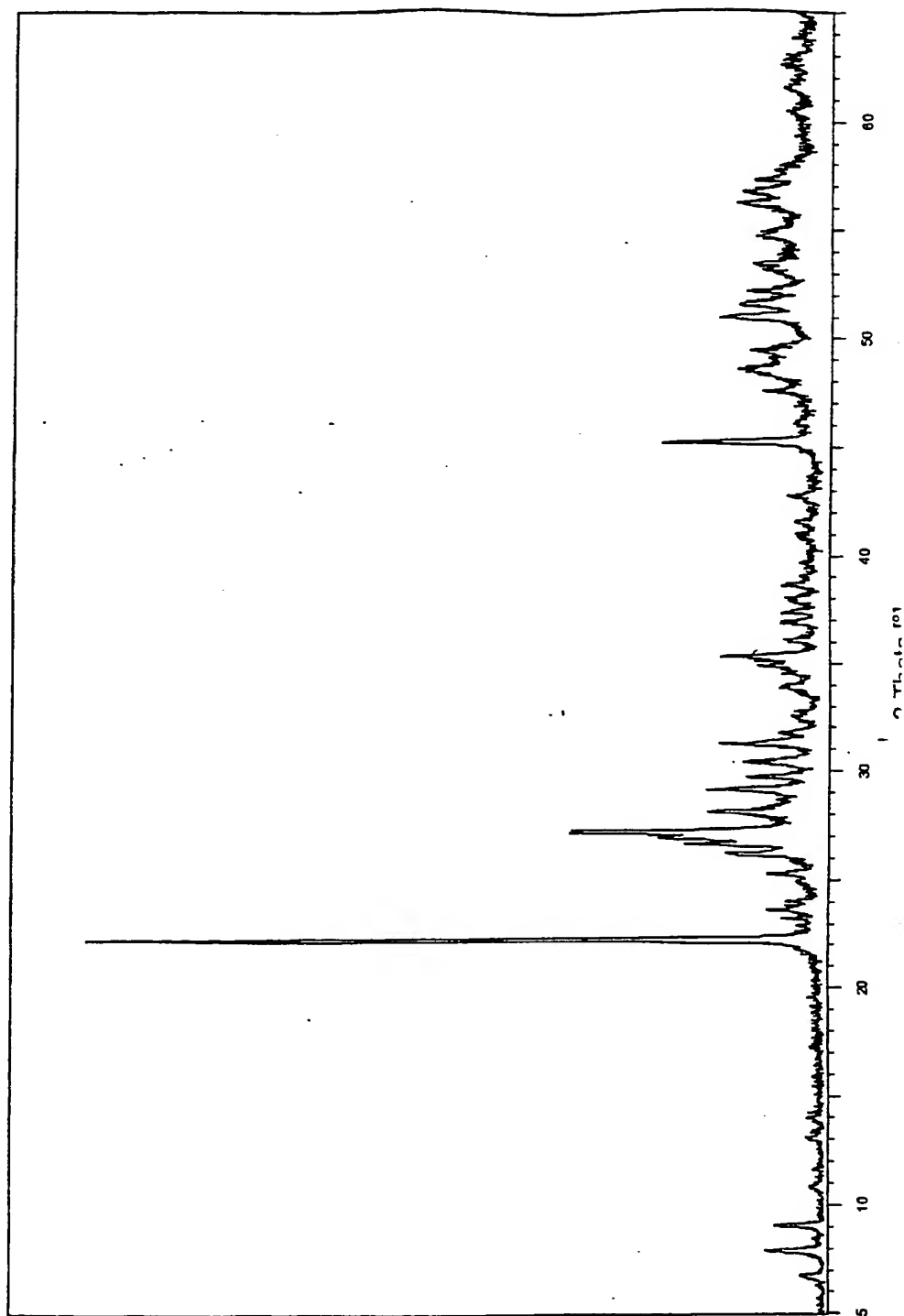


Fig. 6

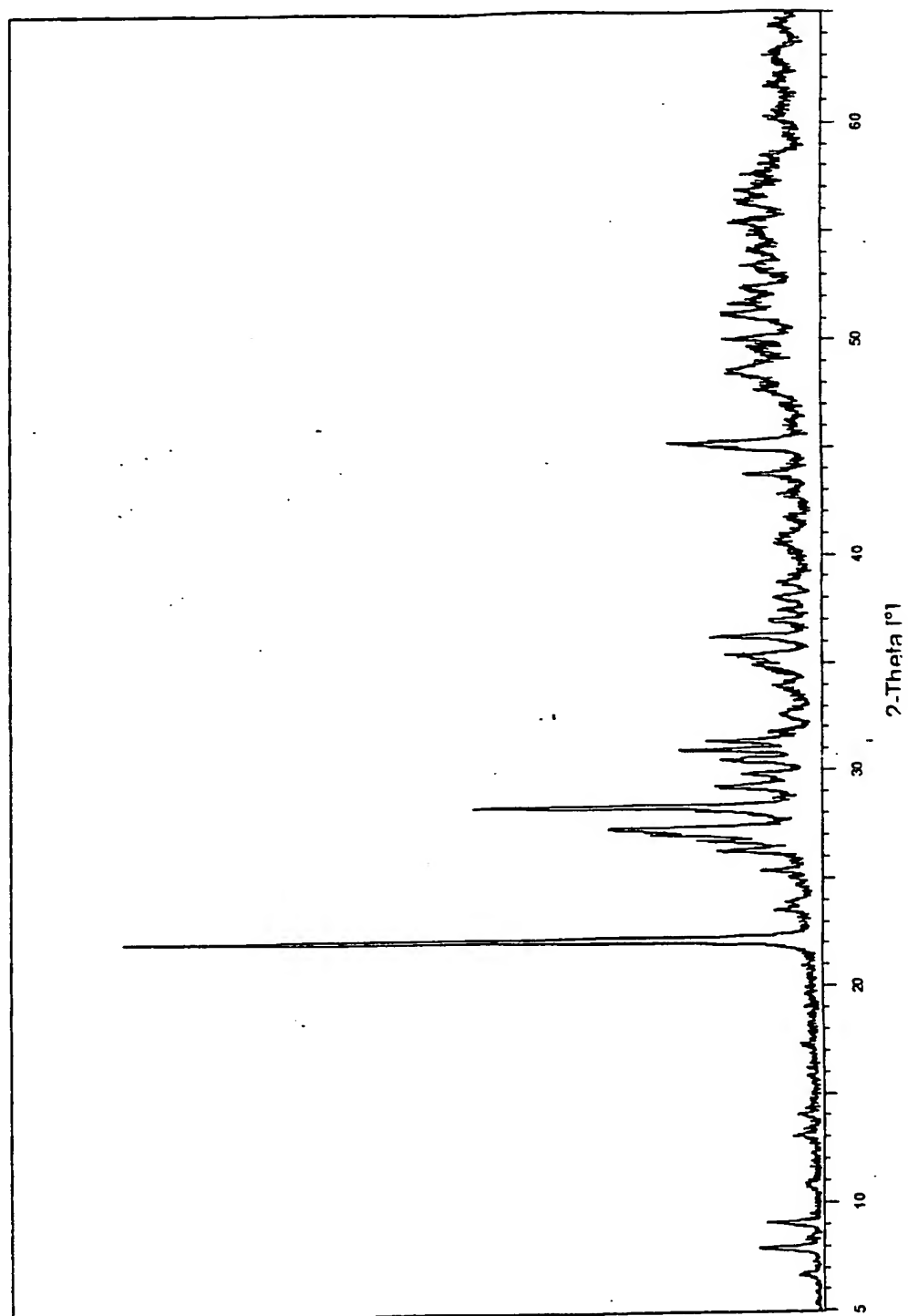


Fig. 7

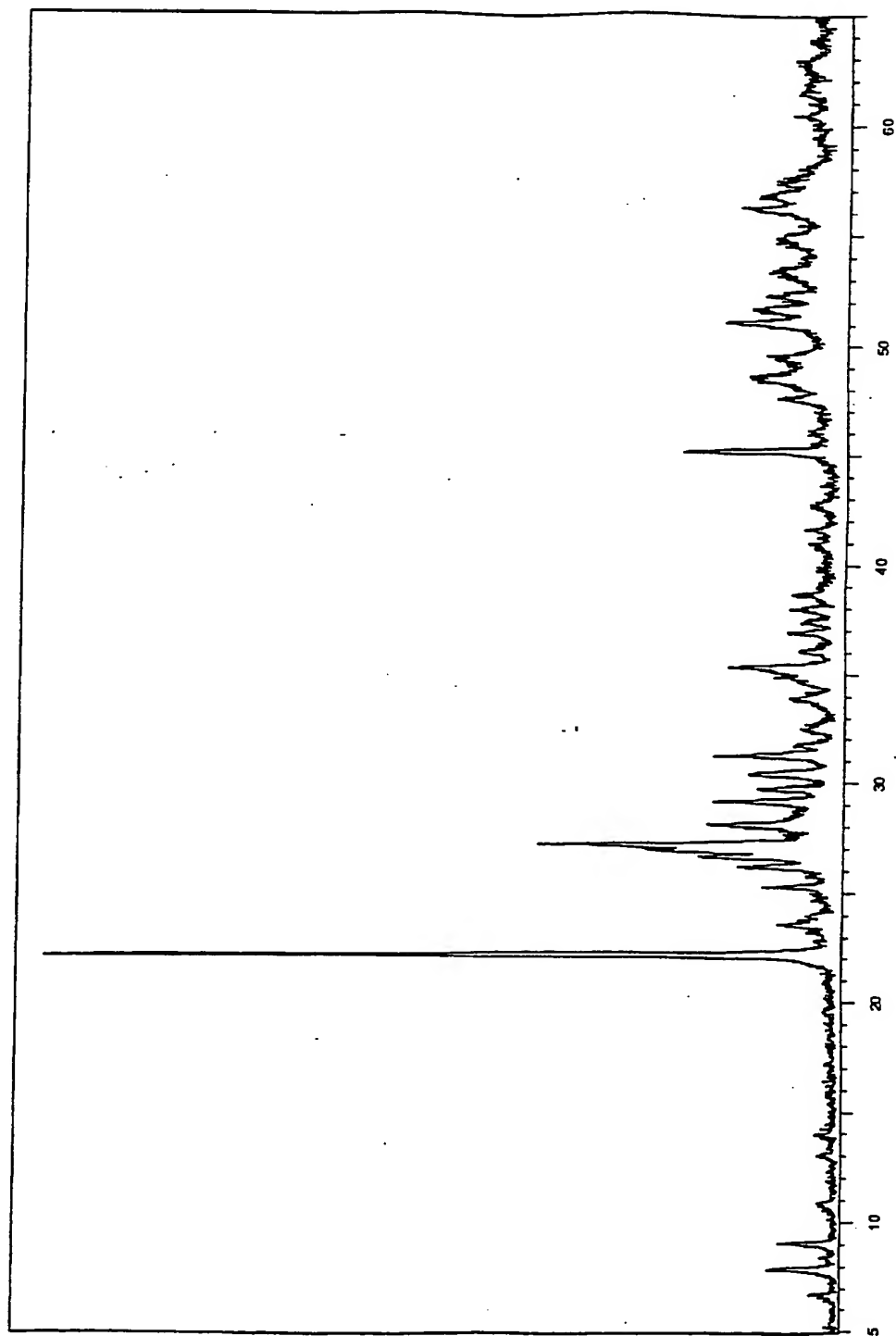


Fig. 8

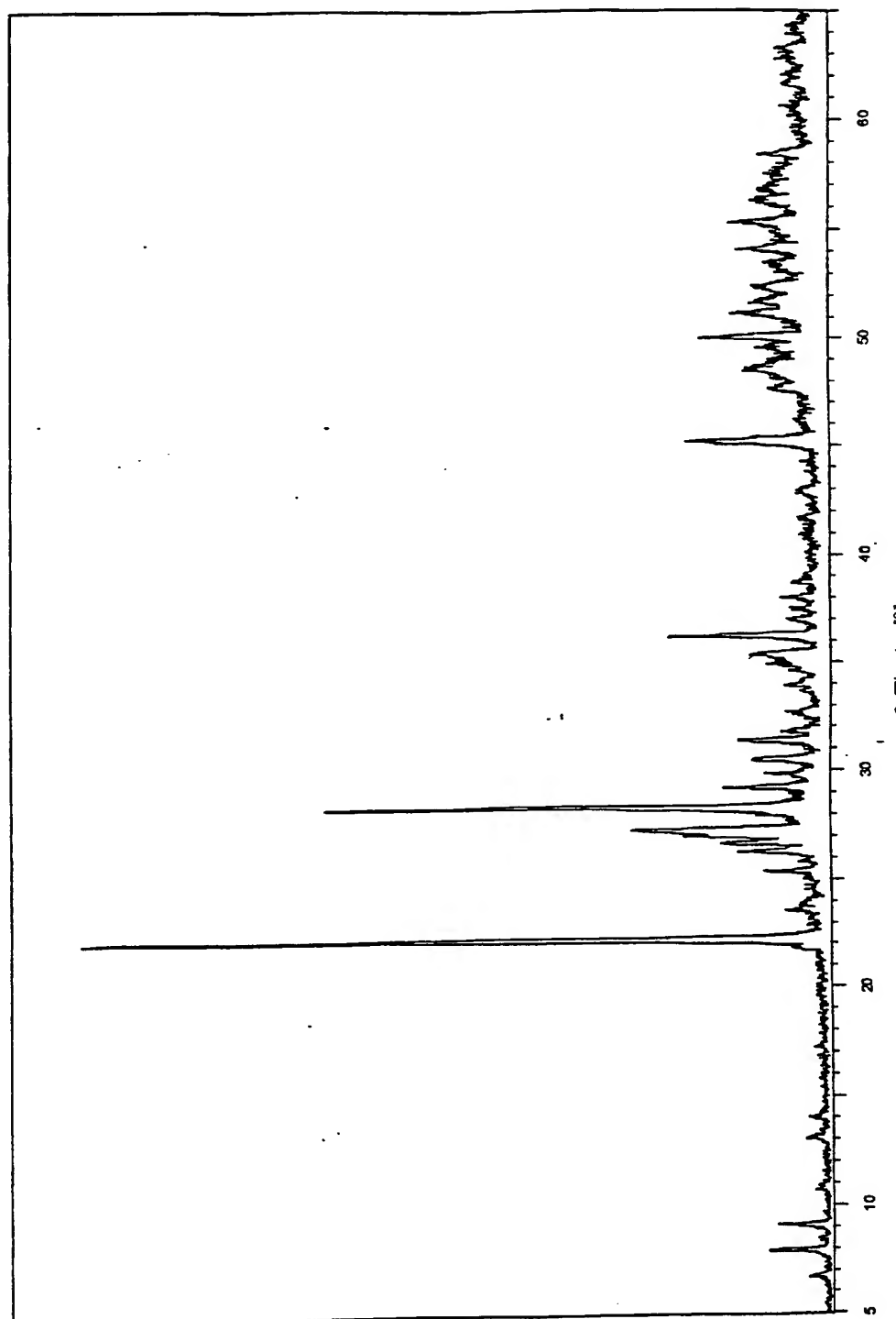


Fig. 9

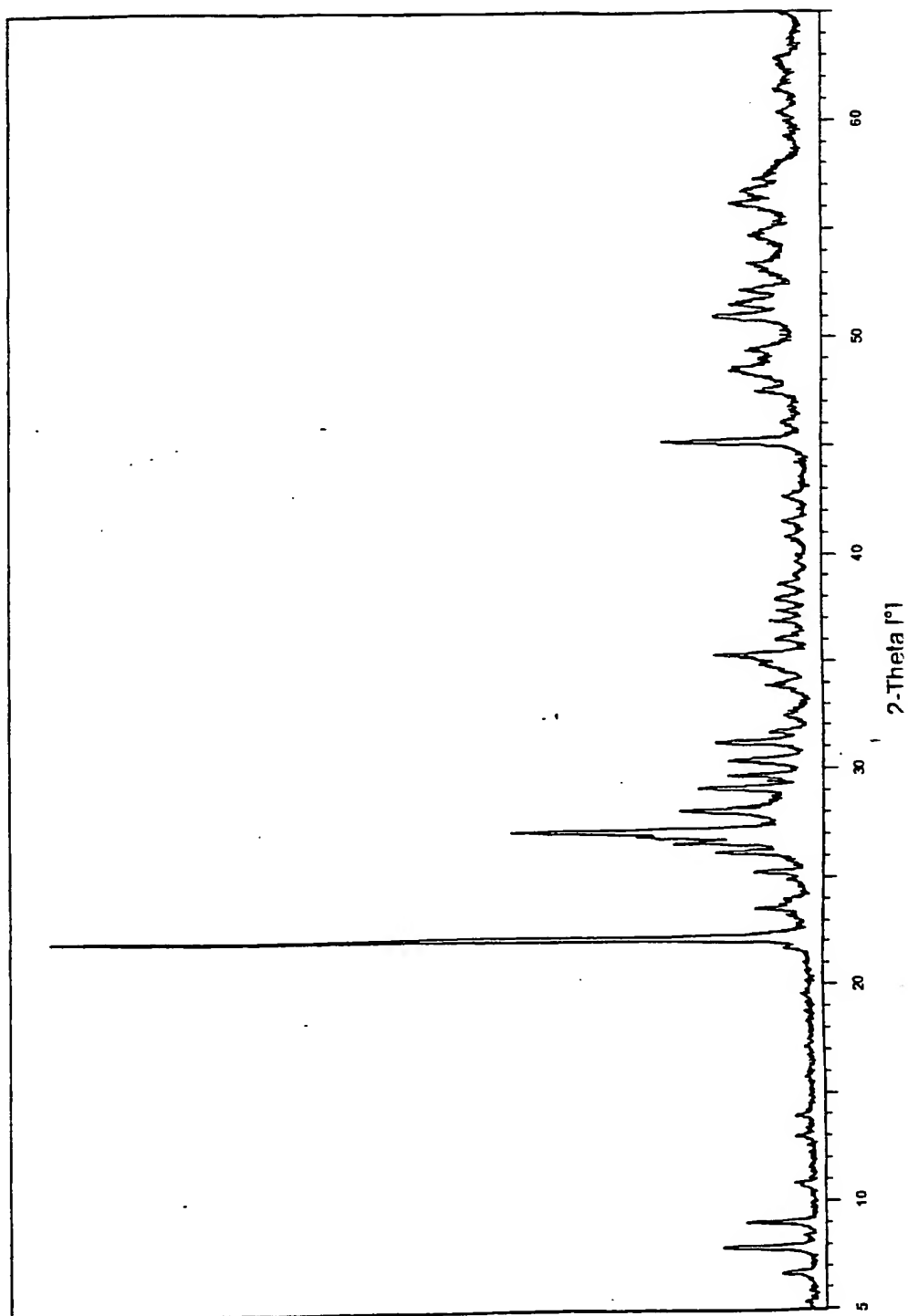


Fig. 10

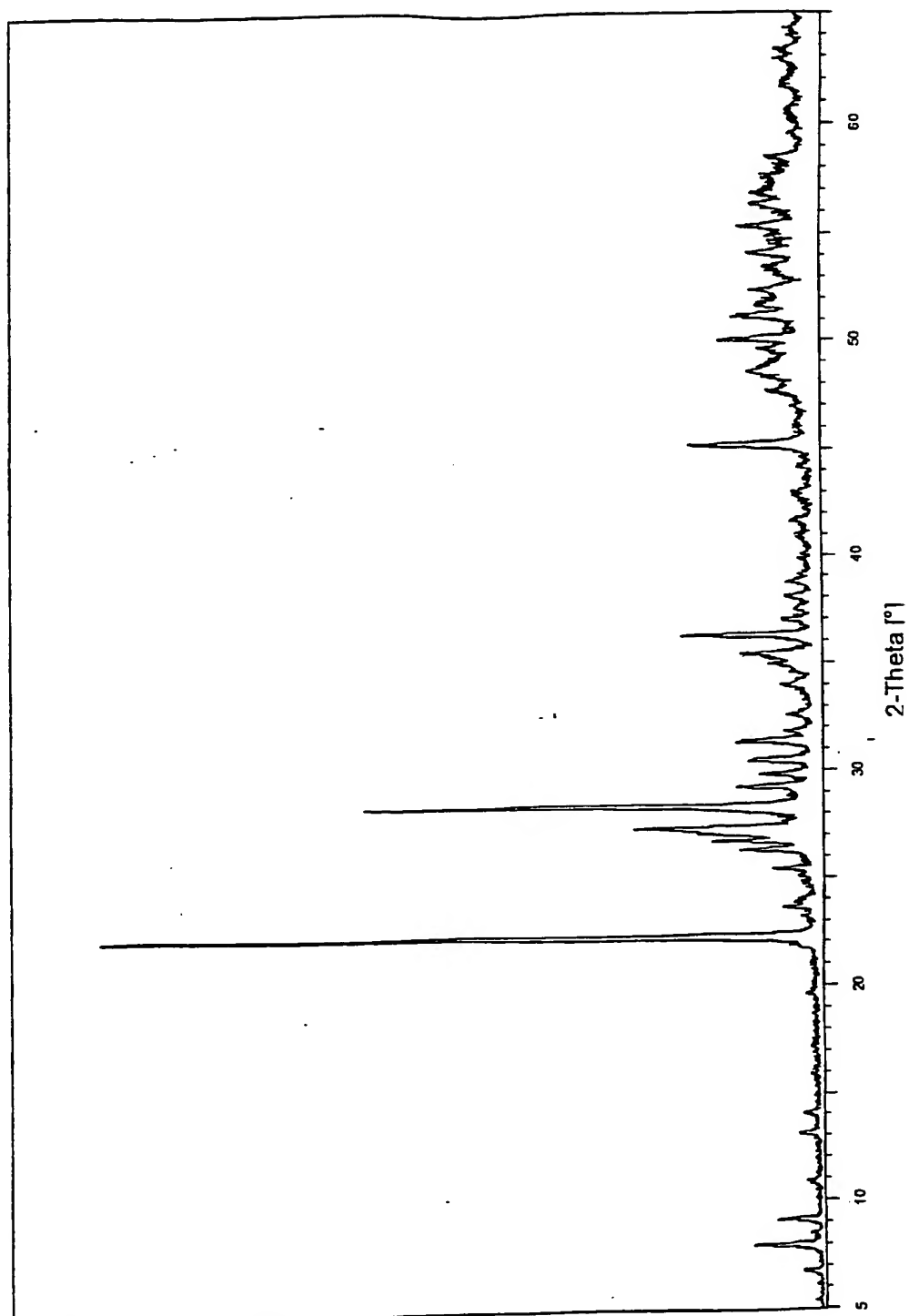


Fig. 11

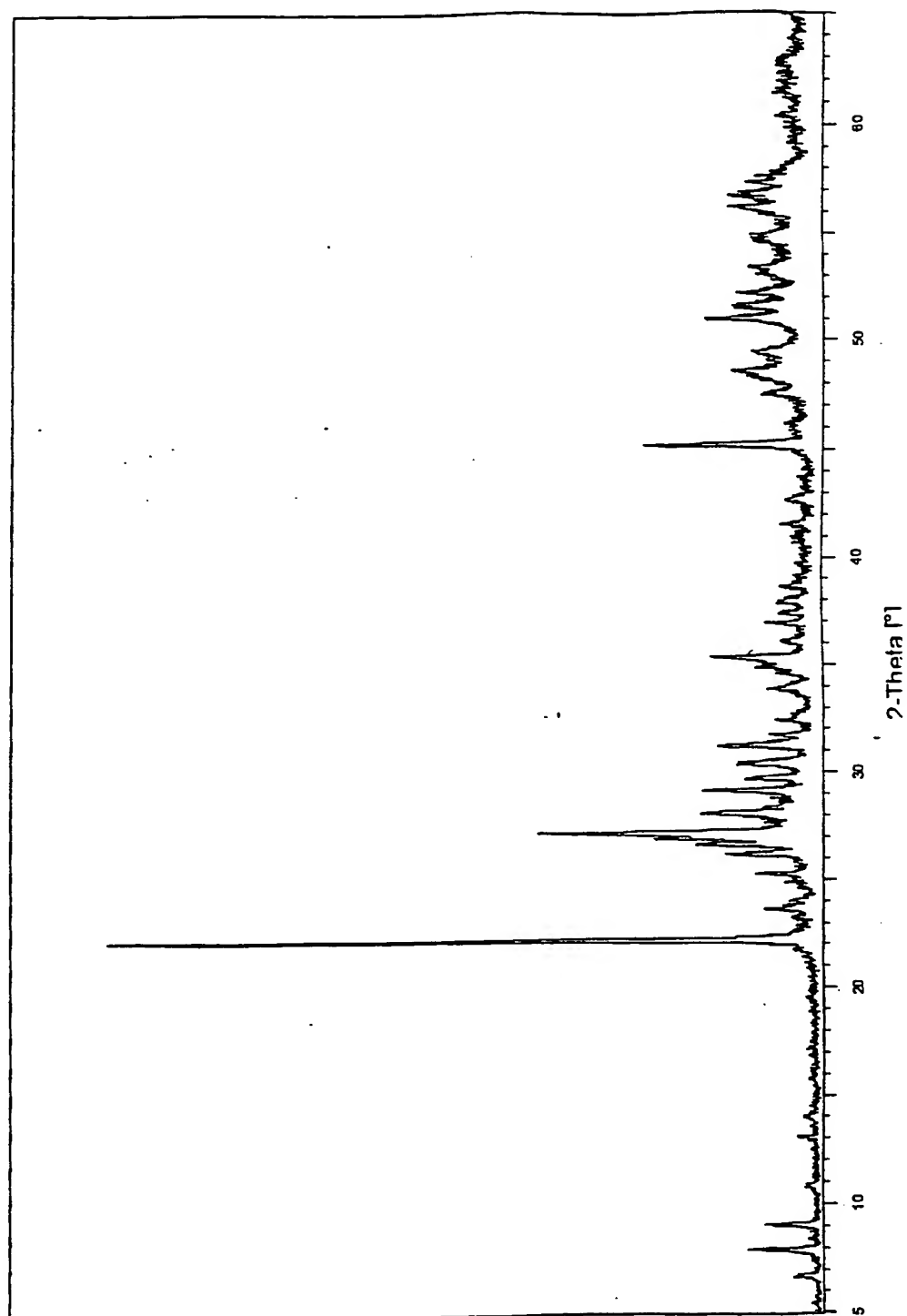


Fig. 12

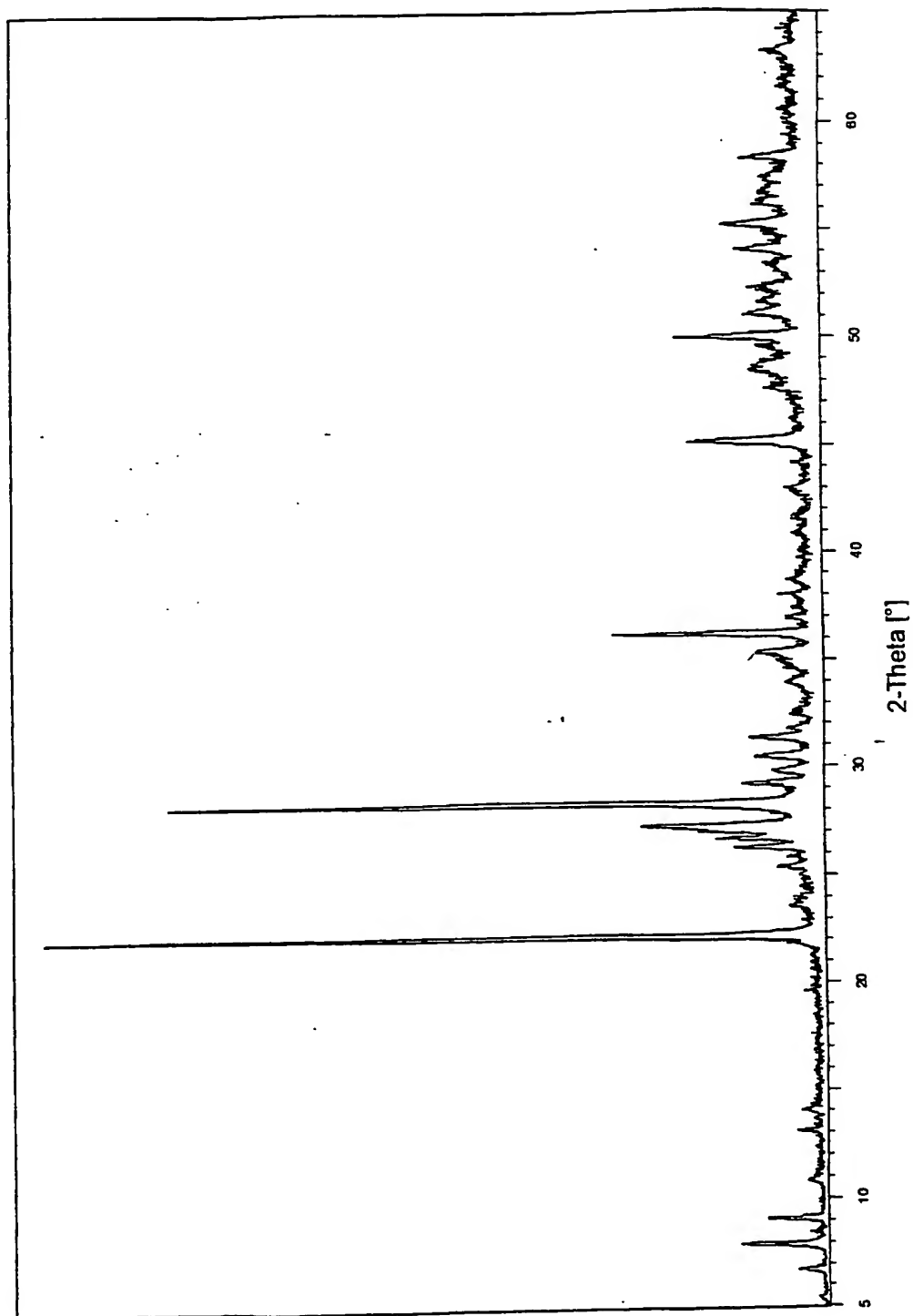


Fig. 13

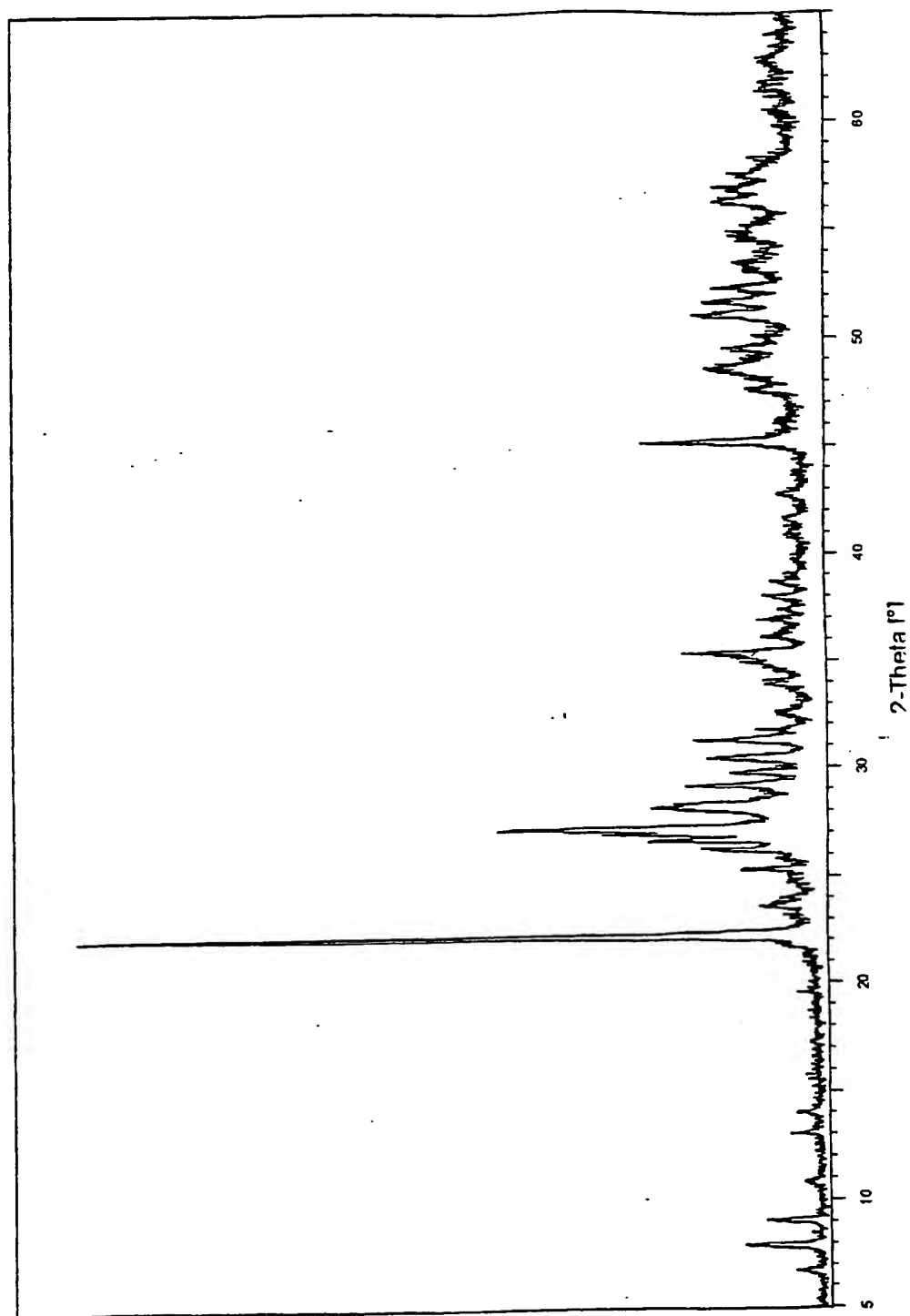


Fig. 14

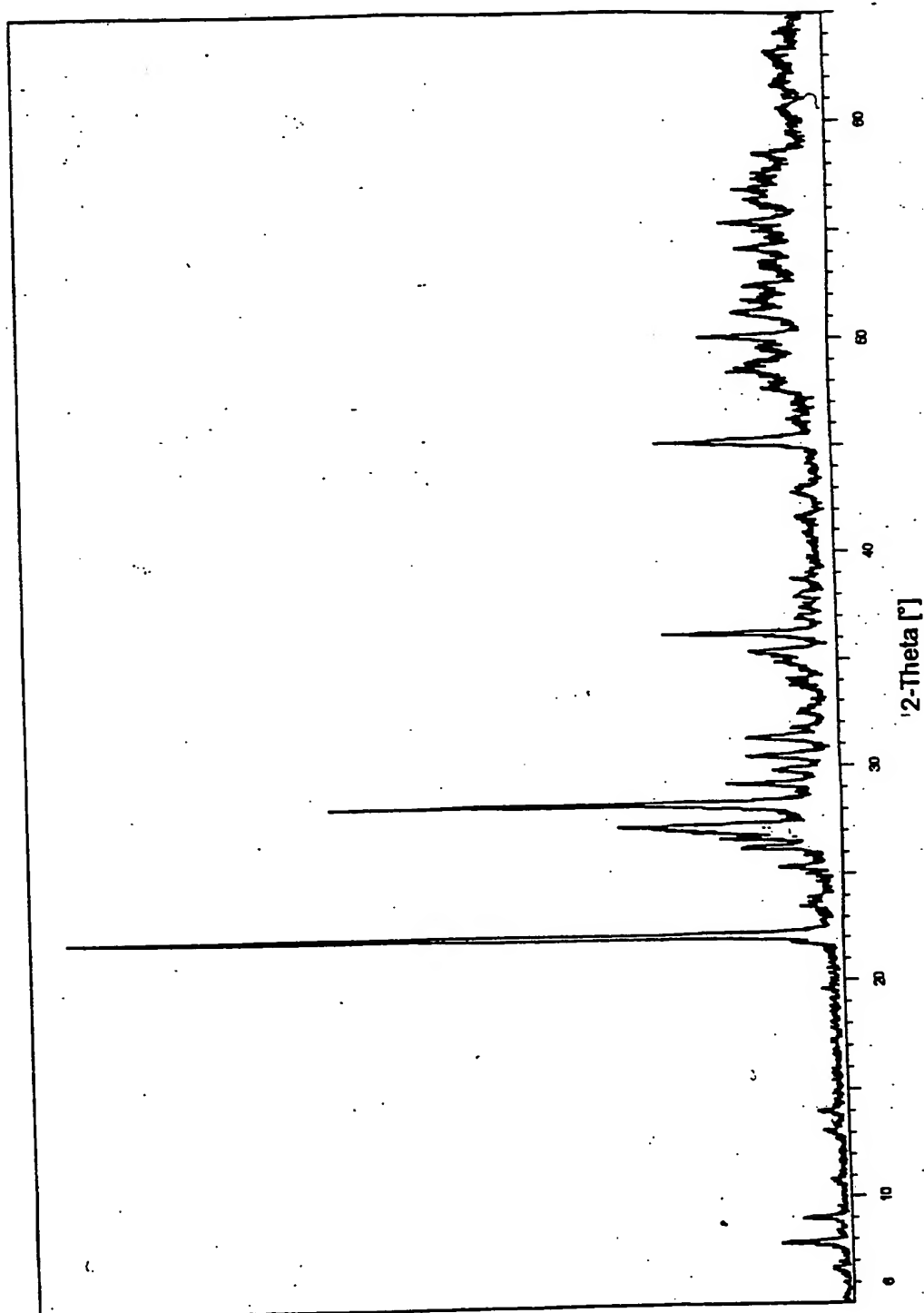


Fig. 15

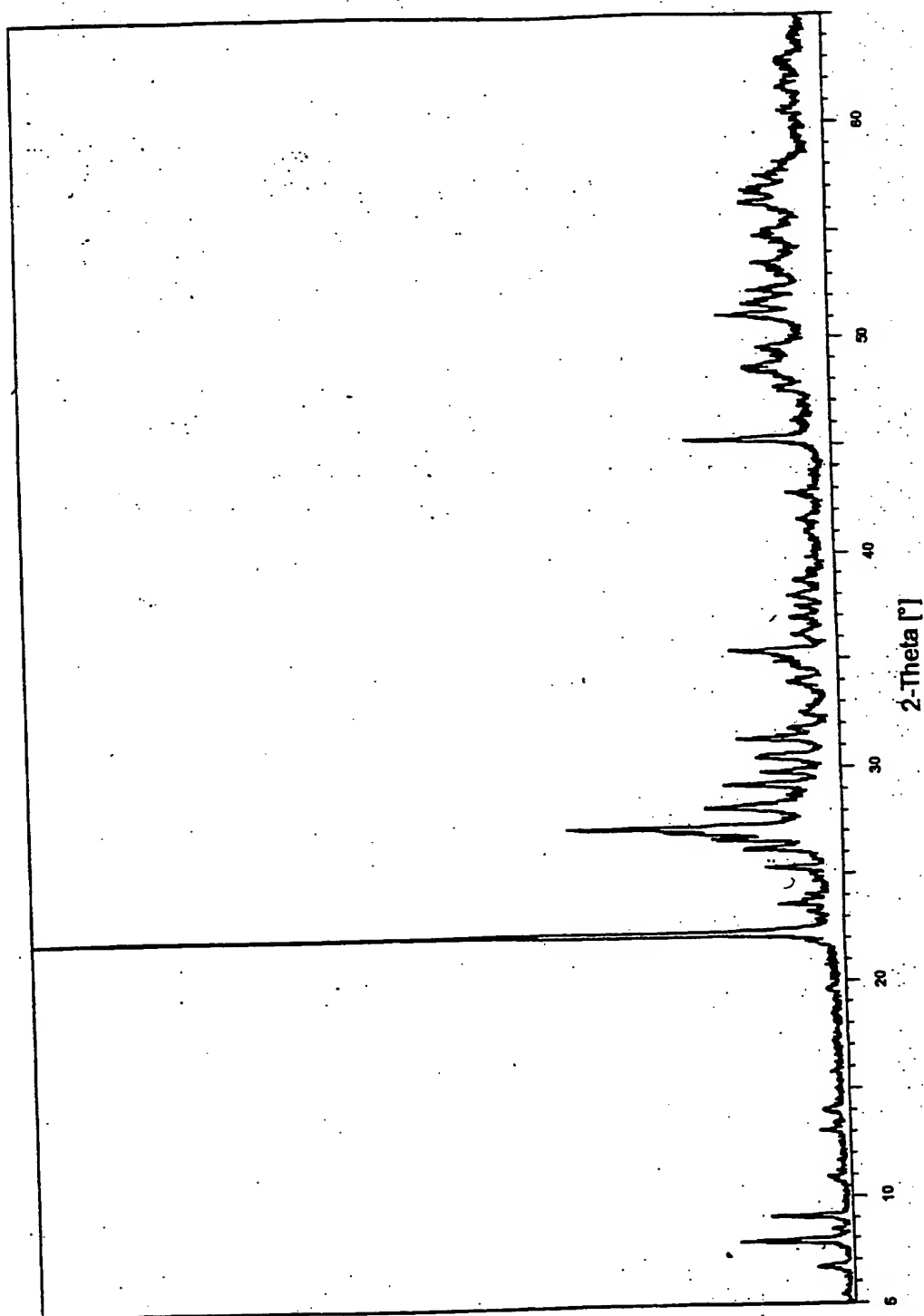


Fig. 16

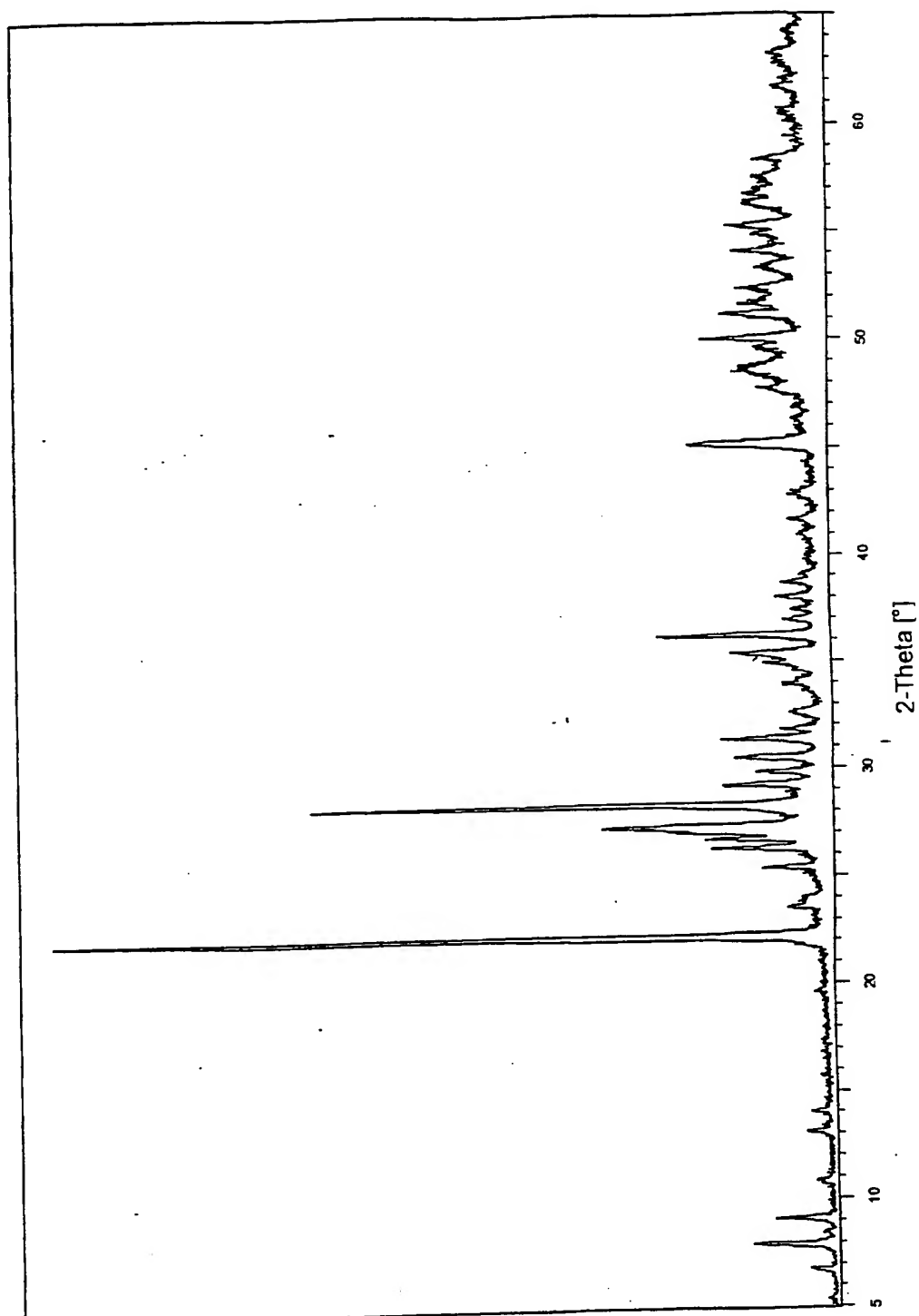
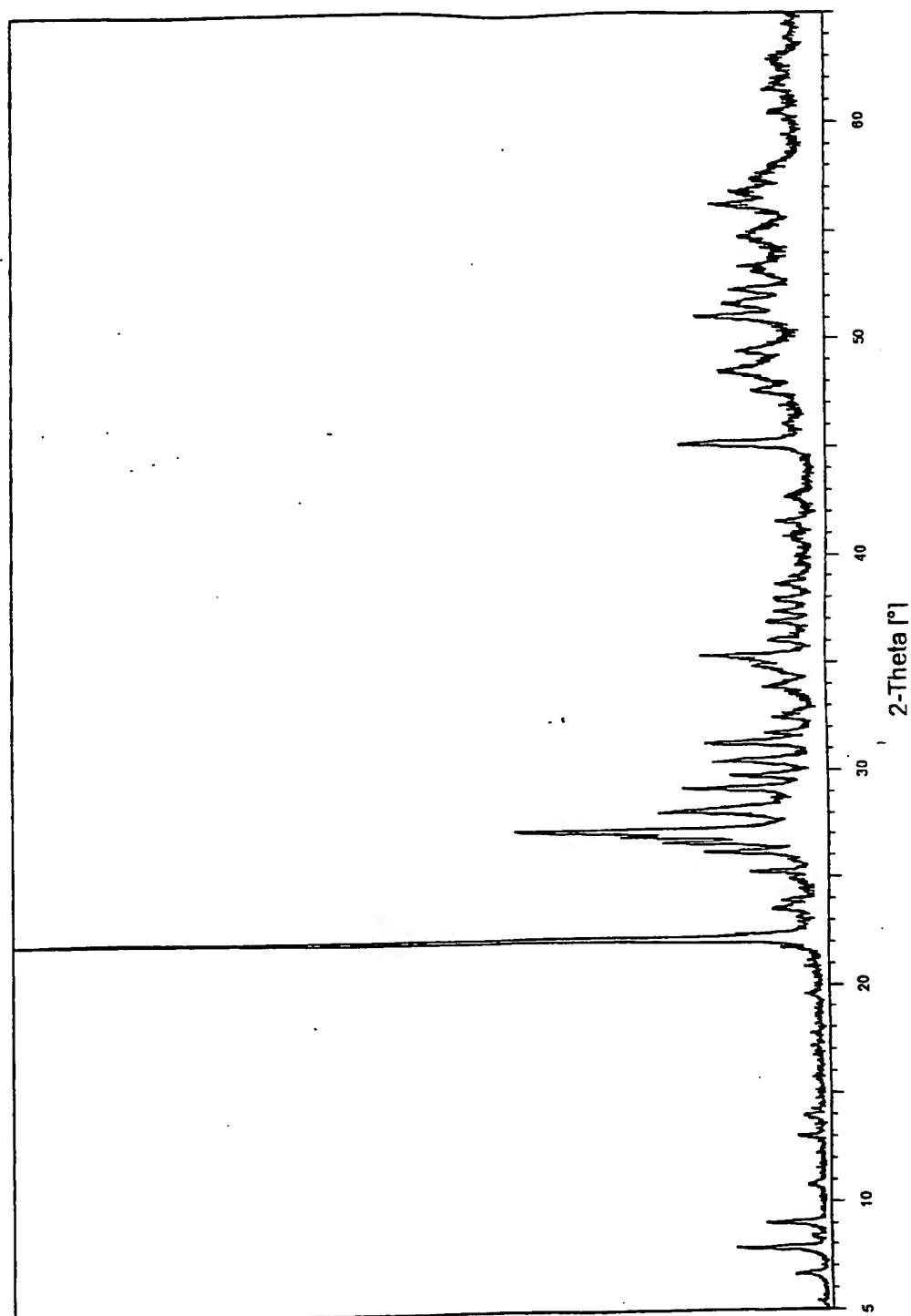


Fig. 17



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